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Quantitative Determination Of Soil And Aggregate Minerals By X-ray Diffraction

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16. ABSTRACT
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The study has disclosed that the diffraction-absorption method is valid for two-component powder mixtures when the mass absorption coefficients of the constituents are close in value. However, for soils which are comprised of many different minerals, absorption effects usually prevent a direct comparison of diffraction peak areas of any given mineral as a function of mineral weight concentration. In addition, corrections must be made for the absorption effects of iron. It was concluded the diffraction-absorption method is too complex for routine analysis of soils.

An interim research project under the direction of Dr. James L. Post was made to evaluate several methods of quantitative analysis and identification by X-ray diffraction. The results of this study showed that a technique of quantifying soils and rocks by using calibration curves best met the need s of the Materials and Research Department. A report titled "X-ray Diffraction Techniques" describes this work.

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STATE OF CALIFORNIA—TRANSPORTATION AGENCY

RONALD REAGAN, *Governor*

DEPARTMENT OF PUBLIC WORKS
DIVISION OF HIGHWAYS
MATERIALS AND RESEARCH DEPARTMENT
5900 FOLSOM BLVD., SACRAMENTO 95819

February 1969
Final Report
M&R No. 632521
D-3-1

Mr. J. A. Legarra
State Highway Engineer

Dear Sir:

Submitted herewith is a research report titled:

QUANTITATIVE DETERMINATION OF SOIL AND AGGREGATE MINERALS by X-RAY DIFFRACTION

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Assisted by

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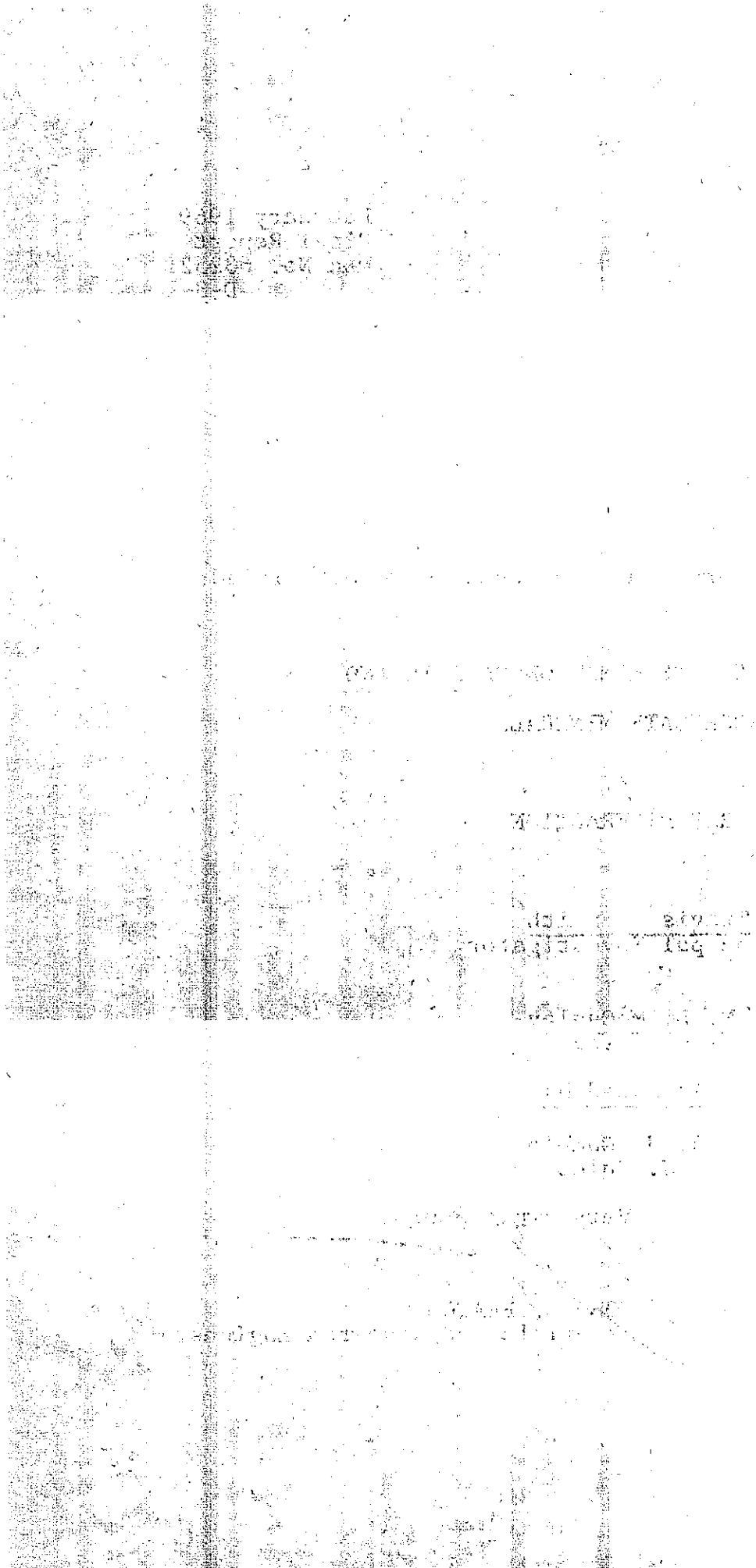
Very truly yours,

JOHN L. BEATON
Materials and Research Engineer



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KEY WORDS: X-ray analysis, X-ray diffraction, minerals.

ACKNOWLEDGMENTS

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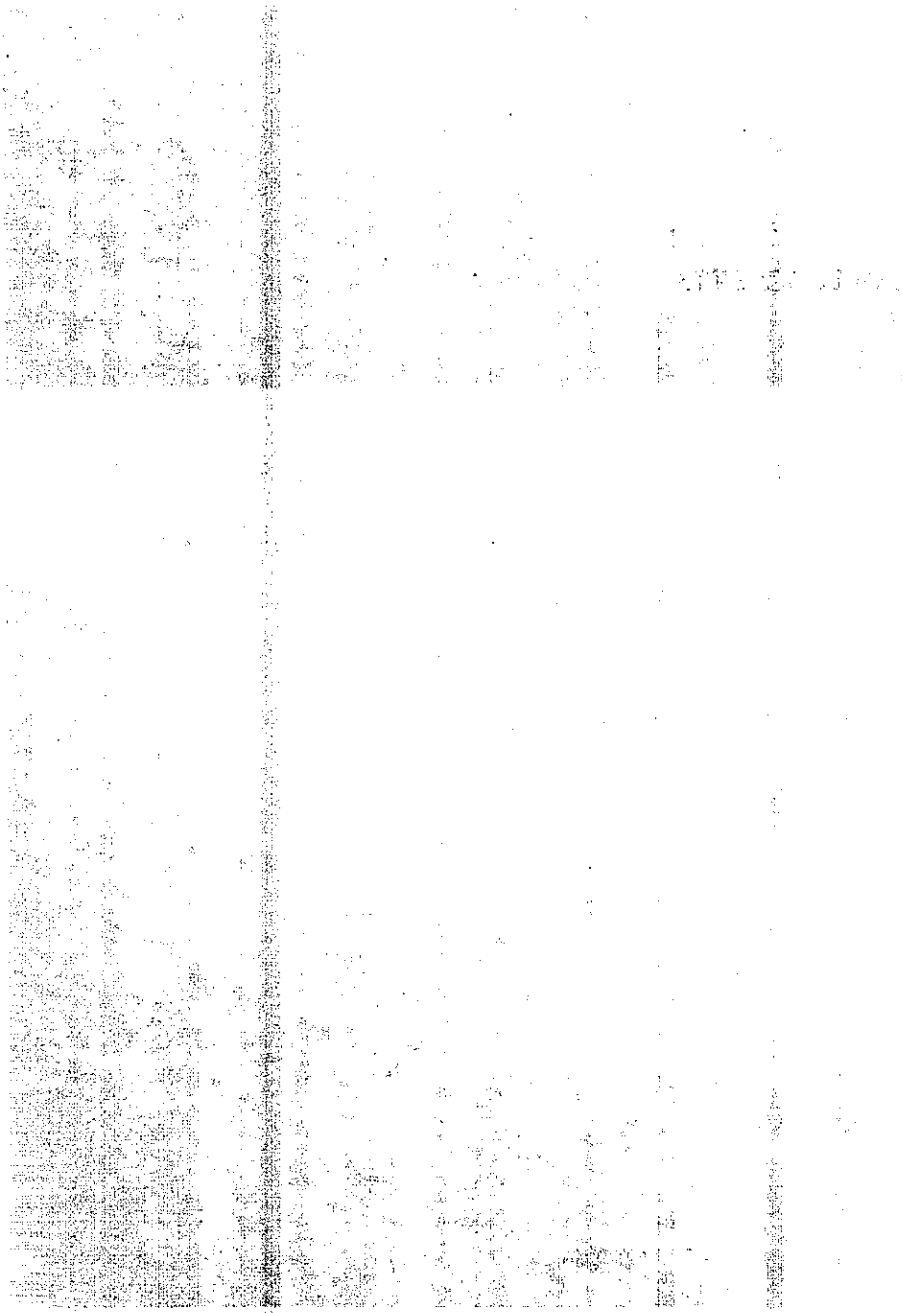

CONTENTS

ILLUSTRATIONS

QUANTITATIVE DETERMINATION OF SOIL AND AGGREGATE MINERALS BY X-RAY DIFFRACTION

INTRODUCTION

The purpose of this research study was to evaluate the X-ray diffraction-absorption method of quantifying the crystalline mineral content of soils and rocks. A practical, reasonably accurate method of quantitative analysis by X-ray diffraction was needed at the Materials and Research Laboratory and the diffraction-absorption technique appeared promising.

A Progress Report* dated September 30, 1965, presents the theoretical equations on which this method of quantitative determination of soil minerals by X-ray diffraction is based, and describes the initial work that was accomplished. The Progress Report also outlines the additional work and equipment needed to complete the project.

In July and August, 1968, a state-financed study was made under the direction of Dr. James L. Post, Professor of Civil Engineering at Sacramento State College, to evaluate X-ray diffraction methods of mineral identification and quantitative analysis. Among the techniques demonstrated by Dr. Post was the method of quantifying soil and rock samples by using calibration curves. As a result of this study, it was determined that the calibration method best met the needs of this department. The report describing the procedures and techniques of mineral identification and quantitative analysis investigated in this study is presented in Appendix II.

Subsequently, in August, 1968, a decision was made to terminate this research project. The principal reason for this decision was the cumbersome nature of this method of quantitative analysis as compared to the calibration method of quantification demonstrated by Dr. Post. This method, as described in Appendix II, is faster and reasonably accurate. The other factors which were considered in making this decision were: (1) the extended X-ray diffractometer time requirements for this research project were beginning to interfere with a continuously increasing routine work load; and (2) similar research by others, e.g., Tatlock, has been published since this project was started.

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*Progress Report on Quantitative Determination of Soil and Aggregate Minerals by X-ray Diffraction, September, 1965.

PART I - PRELIMINARY WORK

Mineral Samples

It was desired that the minerals be obtained from widely separated localities in California, and insofar as possible this condition was met. Because of difficulty in obtaining nearly pure samples of California minerals in sufficient quantity within a reasonable amount of time quartz, feldspar, gypsum, pyrite, and kaolinite were selected for use. A total of 24 samples, each from a separate locality, were collected from 18 counties - ten in northern California and eight in southern California.

A few of the samples are from commercial deposits, but most are from small deposits encountered during routine geologic work, or from highway construction sites. Pure pyrite was the most difficult mineral to obtain, and only four of the pyrite samples collected were sufficiently pure to be used for this study. All of the gypsum samples were selenite, and one of the quartz samples was quartzite. The feldspar samples were all perthitic microcline. A list of the mineral samples and localities is given in Table 1, Appendix I.

Chemical Analysis

A chemical analysis was made of each sample so that the theoretical mass absorption coefficient could be calculated. The analyses are given in Table 2, Appendix I.

Preparation of Powder Samples

All of the samples used on this project were wet-ground with a Fisher motor-driven pestle and mortar under a vapor hood. The hood was necessary because butanol was used, as the liquid grinding medium. Wet grinding was used, at the suggestion of Dr. Robert Rex*, for the purpose of obtaining more uniform particle size.

First, the mineral samples were ground in a ceramic mortar and pestle by hand to material passing a Number 60 sieve. Then 12-15 grams of the material passing a Number 60 sieve were ground in the Fisher grinder. After about 15 minutes grinding time (depending on the mineral) the fine material held in suspension was carefully removed by pipette and dried in a shallow pyrex dish at 140°F. This process was continued until the required amount of material was ground. Essentially all of the powder ground in this manner passed a 325 mesh sieve (44 microns).

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*Chevron Research Company, La Habra, California

For each of the 24 mineral powders, 10 two-component mixtures (pentaerythritol and mineral) were to have been prepared at 10% increments of mineral concentration from 10 to 100%. The two components were weighed to .0001 gram to secure an accurate mixture in each sample. To insure thorough mixing each powder concentration was to have been rolled overnight on a paint roller. The study was terminated before all of these mixtures had been prepared.

Back-Pack Fabrication Machine

The essential parts of the back-pack fabrication machine are a circular turntable and a screw-type press mounted on a sturdy rectangular hardwood base. A fixed holder on the turntable places the back-pack assembly under the Syntron vibrating unit (described in Progress Report); after the excess powder is removed the back-pack assembly is brought into position precisely under the press by rotating the turntable. The foot on the press exactly fits the opening in the back-pack frame. The press is turned by hand to lower the foot to a position that coincides with the top surface of the back-pack frame; this position is controlled to a tolerance of $\pm$.001 inch by a spacer ring. The amount of powder that is pressed into the back-pack frame is controlled by aluminum templates of varying thickness. The density of the powder determines the thickness of the template that is used; a single template will serve satisfactorily for quite a broad range of powder density.

The mineral powder is pressed into the back-pack frame against a frosted glass slide, and the top surface of the powder is covered by a strip of transparent tape. This same strip of tape also holds the glass slide securely in place until the slide is removed just before making the X-ray scan. The back-pack fabrication machine is shown in Figure 1, page 4.

Back-Pack Frames

The back-pack frames were made from aluminum to the following dimensions: 2 inches long x 0.561 inch wide x 0.0625 inch thick. The volume of the powder cavity is 1.136 cu cm. This volume was increased slightly by the use of frosted glass slides. The average volume of the cavities in the glass slides was determined to be 0.016 cu cm giving a total volume of 1.152 cu cm.

Frosted Glass Slides

The frosted glass slides were fabricated from 75 x 25 x 1 mm microscope slides. The close tolerances of the back-pack machine required that the slides be of uniform thickness; this was achieved by micrometer measurements made at several places on each slide. The slides to be used were secured in a metal holder that exposed the correct area, and then sandblasted. Each slide was inspected visually during the sandblasting process to insure a uniform degree of roughness for the set. These frosted slides were used to fabricate all of the powder samples used on the

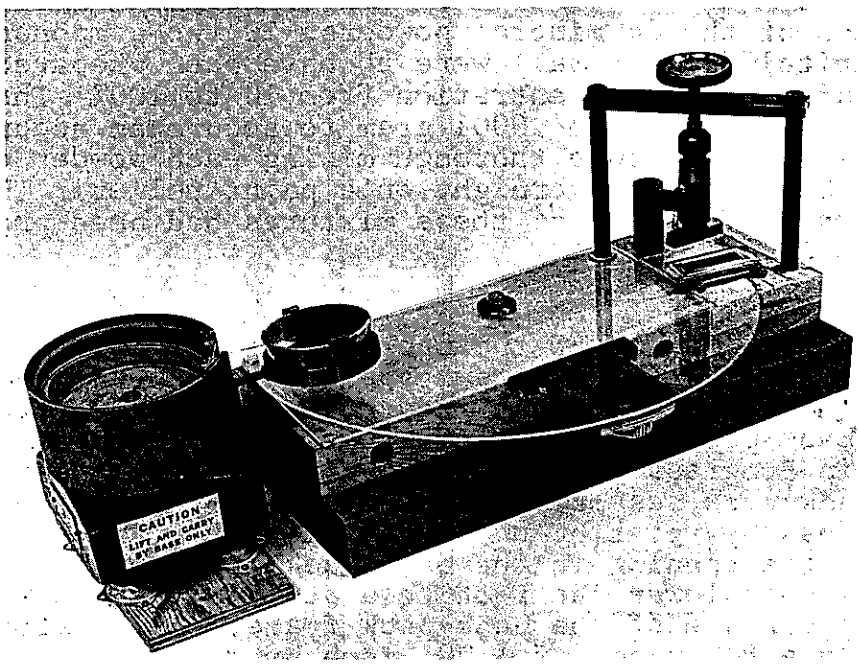


Figure 1

Back pack fabrication machine

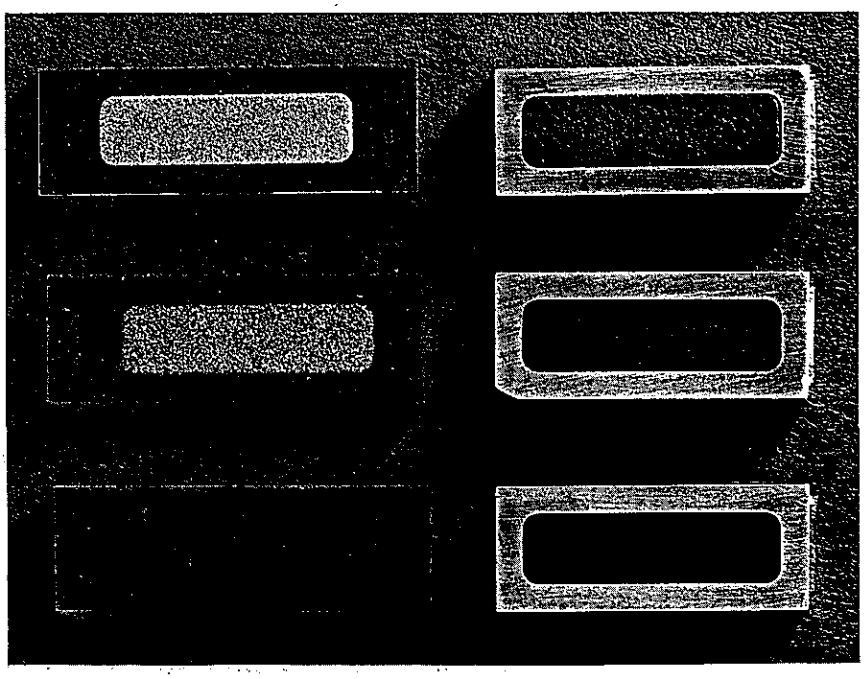


Figure 2

Smooth, moderately frosted, and intensely frosted glass slides and the corresponding surfaces impressed on the samples.

research project. A smooth, moderately frosted, and intensely frosted slide, and the corresponding surfaces impressed on the samples are shown in Figure 2, page 4.

Aluminum Foils and Foil Selector

The foil selector holds a total of 99 aluminum foils fixed in two rotating brass disks in such a manner that any number of foils from 1 to 99 can be rapidly selected and positioned in the X-ray beam. The design incorporates a sample holder, and a safety gate that can be closed so the sample can be inserted and removed without shutting off the X-ray tube. The foil selector is mounted to the beam slit bracket as shown in Figure 3, page 6. Figure 4 is a close-up view of the counter side of the foil selector with sample holder. A disassembled view of the foil selector is shown in Figure 5. The gate mechanism is shown at upper left and a punch press for cutting the aluminum foil disks at upper right of the photograph. The aluminum foils were made from very pure, 0.0003 inch thick aluminum sheet obtained from Tem-Press Research, Inc.

In order to determine if the alignment stability was reasonably constant, periodic intensity readings were taken on a foil pack for a 10-hour period. During this time interval the tube was operated continuously without making any adjustments. It was noted that following a 1½-hour "warm-up" stage a "maximum" intensity was reached. But subsequently the diffracted intensity decreases. A plot of this data is shown in Figure 1, Appendix I.

To determine if the diffracted intensity was a linear function of foil thickness, combinations of thicknesses from 1 to 99 were X-rayed. The 99 possible combinations were X-rayed in random order to minimize systematic errors due to alignment stability. A plot of the resulting data is shown in Figure 2, Appendix I. The data show an appreciable scatter. This scatter is due to the gradual change of incident beam intensity with time, and to electronic noise. The rate of intensity change was approximately 500 cps/hour after the "maximum" intensity was reached. The average noise level was 4 cps.

To compensate for this change in incident beam intensity with time, an intensity reading was taken on a standard 40 foil. This intensity reading was then compared to the intensity for the maximum value obtained previously. The ratio of these values (see sample calculation p. 7) was used to correct the intensity value of an unknown to the value it would have been if the initial incident beam intensity had remained constant. Figure 3, Appendix I, shows a plot of the same data of Figure 2, Appendix I, corrected for intensity changes.

It was noted (refer to Figure 6) that the beam intensity changes with time. To compensate for intensity changes the following equation was developed:

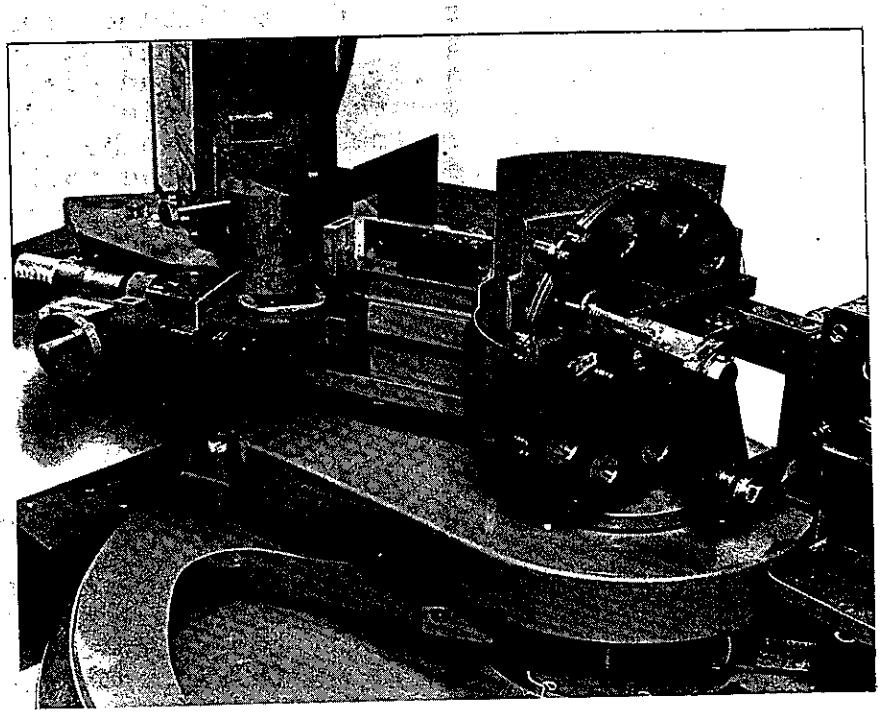


Figure 3

Aluminum foil selector mounted to the beam slit bracket

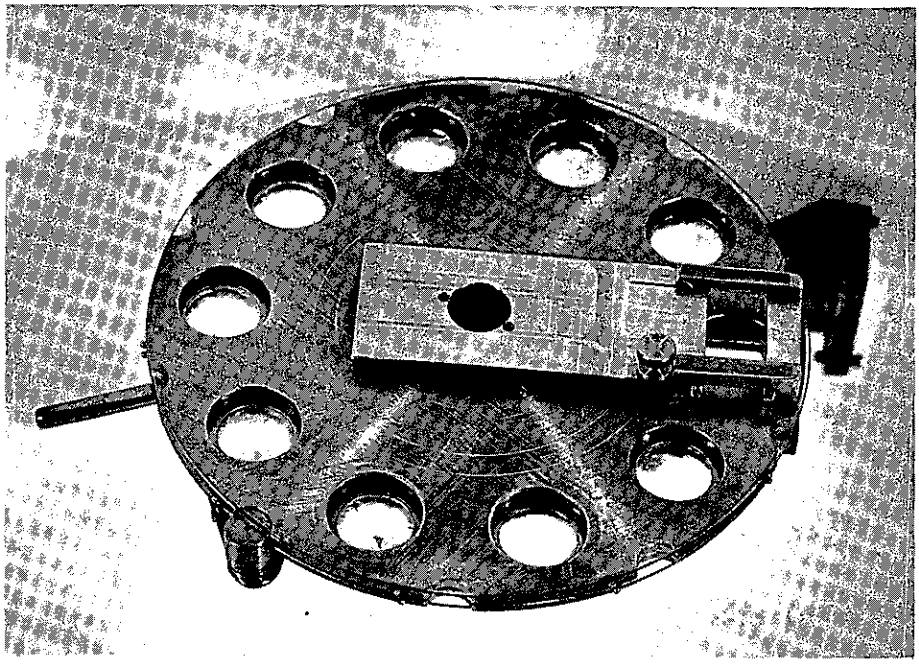


Figure 4

Close-up view of the aluminum foil selector with sample holder. When mounted the side shown is toward the counter.

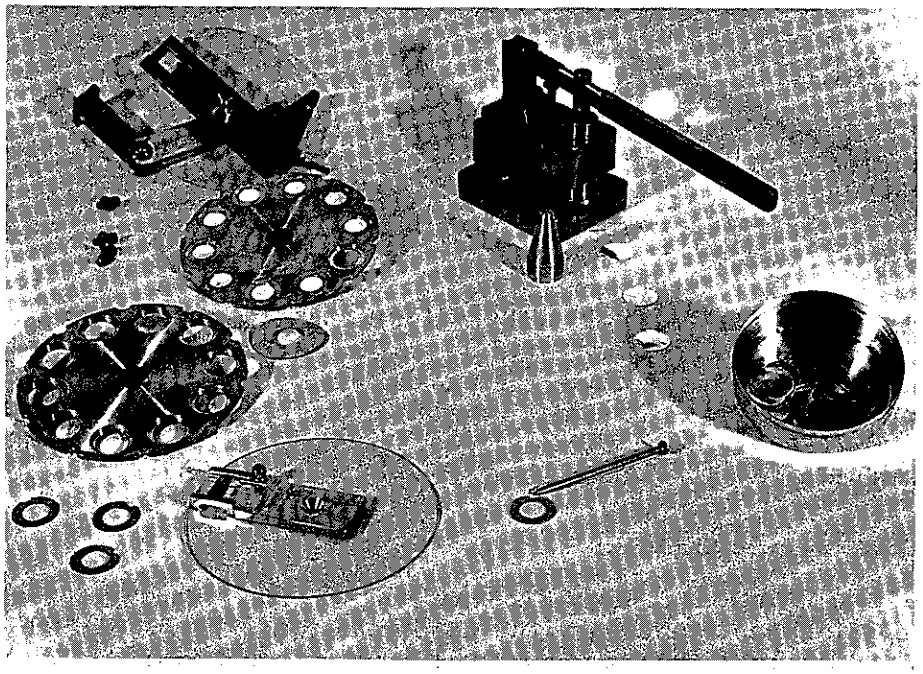


Figure 5

Dissembled view of the aluminum foil selector. The gate mechanism is shown at upper left; a device for cutting the aluminum foil disks is at upper right.

$$I_{corrected} = (S-N)\frac{A}{A^1} \qquad (1)$$

Where: $\frac{A}{A^1}$ - is the ratio of the intensity for a standard 40 maximum value to the intensity of the same standard 40 taken immediately before the intensity of the unknown (S).

S = uncorrected intensity of the unknown

N = noise

For example, refer to foil No. 50 in Figure 2.

S = 37.9, N = 4 (from Fig. 2).

A = 8260 cps (from Fig. 3).

A^1 = 5350 cps (taken prior to S).

Then: $\frac{A}{A^1} = \frac{8260}{5350} = 1.544$

$\therefore I_{corrected} = (37.9 - 4)\ 1.544 = 52.2$ cps

PART II - X-RAY PROCEDURE

Diffraction Pattern

A diffractogram is made from 3 to 63 degrees 2θ from which the areas under the selected peaks can be determined (Fig. 12, Progress Report).

Machine Settings

A General Electric XRD-5 X-ray machine, using a high intensity X-ray (copper) tube, a General Electric monochromator with a lithium fluoride crystal, and a SPG-3 counter was used. The machine settings used were KVA-50, MA-40, HVA-6.5, 1000 CPS, TC = 0.5, Slits 3°/0.04°/MR, take-off angle 3°. The scan rate was 4° min.

Mass Absorption Coefficient

The mass absorption coefficient of a soil sample is determined by measuring the mass absorption coefficient of the total thickness of the added aluminum foils (#) which is equivalent to the mass absorption coefficient of the sample.

Machine Settings -

1. Same as above for diffraction pattern.
2. Gonimeter set at 44.94° (2.015Å).
3. LiF analyzing crystal in regular sample holder.
4. Aluminum foil selector attached to beam slit holder (refer to Fig. 3).
5. Sample mounted in the sample holder attached to the foil selector.

Procedure -

1. For control purposes take a count on the standard 50 aluminum foils.
2. With a soil sample in place add 99 foils (aluminum foil selector) as a first trial. Then proceed to decrease the number of foils until the counter registers a minimum of 10,000 counts. A maximum counting time of 15 minutes is used. When a 15 minute count time does not give a 10,000 count level the sample is refabricated using a lower density to yield a higher count per unit time.
3. A background reading is then obtained by closing the gate (attached to the rear of the aluminum foil selector) and counting for 10 seconds.
4. Remove the soil sample (while the gate is closed) and then register the standard 50 aluminum foil in the foil selector. Open the gate and take the normal standard 50 count.
5. With gate open begin to "match counts" (same as obtained in step two) by adding a sufficient number of foils (# of equation 4) so that the resulting intensity is nearly equal to the intensity obtained in step two.
6. Repeat step three.
7. Make sure that the error is within the limits of $\pm$5% of the theoretical value (when using a known mineral sample). In those cases where the experimental mass absorption deviated by more than $\pm$5% from the calculated theoretical value, another sample was fabricated, and a new value obtained, which in most cases would be within the desired limits of error. It was necessary to obtain a second mass absorption value for four of the 10 two-component gypsum samples. Some possible reasons for this kind of error are differential sorting, and particle orientation.

PART III - CALCULATIONS

Calculating the Mass Absorption Coefficient

The mass absorption coefficient is determined by substitution in equation four of the Progress Report:

$$\mu_T = \left[\ln \frac{I'}{I} - \mu_{Al} \rho_{Al} (t_{Al} - t'_{Al})\right] \frac{1}{\rho_T t_{Al}}$$

To simplify computation this equation can be written

$$\mu_T = \frac{X - \mu_{Al} \rho_{Al} (\#)}{(\rho_T) t_{Al}} \qquad (4)$$

Where: μ_{Al} (mass absorption of aluminum)* = 49.6

ρ_{Al} (density of aluminum)* = 2.668 gm/cm^3

t (thickness of sample) = 0.1614 cm

ρ_T (sample bulk density) - calculated

I - count without sample, but with additional aluminum foils to match.

I' - count with sample in place

$\frac{I'}{I} = e^x$ - values of x from table of exponential functions. The value of the ratio $\frac{I'}{I}$ kept very close to one.

\# - the total thickness of aluminum foils (number of foils times average thickness) added in place of the sample to bring the total counts to the same intensity level as was obtained for the sample.

Calculating the "k" value

The "k" values for the sample can be found by substituting the values for the mass absorption coefficient in equation 2a (p. 2, Progress Report):

$$k_i = \frac{I_i \mu_T}{x_i} \qquad (2a)$$

*Aluminum foil (99.3% Al) from Tem Press.

Where: I_i = the diffracted intensity of the i^{th} component in cps (area under a selected peak).

μ_T = Mass absorption of total sample.

x_i = The weight fraction of the i^{th} component.

Experimentally, a range of "k" values is obtained for the mineral, and these values are plotted against the percent of mineral present in the sample. The particular "k" value selected from this range for quantitative purposes is the value obtained for the 50% level. The amount of the mineral present in the sample is found by substituting this "k" value in equation 2b (p. 2, Progress Report):

$$x_i = \frac{I_i \, \mu_T}{k_I} \qquad (2b)$$

Where: k_i = "k" value of the i^{th} component.

Experimental mass absorption coefficients were obtained for each of the 10 two-component powder mixtures (see p. 3) for quartz Sample 700-1. However, six of these values were not within the ±5% limits of error and before a new set of mass absorption values could be determined a malfunction of the counter tube necessitated its replacement. It was decided to terminate the project during the six weeks delay that ensued and a complete set of data for quartz was not obtained. No experimental mass absorption coefficients were obtained for the other mineral samples.

The attempt to obtain mass absorption coefficients for pyrite was unsuccessful due to minute cracks appearing in the sample after it was pressed into the back-pack frame, or the sample crumbling completely when inserted into the X-ray machine sample holder. Doubtless these difficulties can be overcome by some means such as spraying the top surface of the sample with plastic, but the work of devising and testing a satisfactory method was not completed.

A complete set of data was obtained for gypsum Sample 3000-1 and plots of the "k" values obtained for the 7.60, 3.80, and 2.88 angstrom peaks are shown in Figure 4, Appendix I. An example of the procedure used to determine the mass absorption and "k" values of the 50% mixture for this same sample is illustrated in Figure 5, Appendix I.

PART IV - PROBLEMS OF QUANTITATIVE ANALYSIS

Serious difficulties are encountered with the diffraction-absorption method when a small amount of iron is present in the sample. Errors in the reported mineral content of up to 25% can result from the presence of as much as 10% Fe_2O_3, as shown by Figure 6 on page 17 of the report "X-ray Diffraction Techniques" in Appendix II. Further, in mixtures of minerals, the peak height variation caused by variation in percentage composition may be a curvilinear function. The basic equation (2b) of the diffraction-absorption method assumes a linear relationship. The effect of the above factors on equation 2b is that I_i and k_i, assumed to be constants, are in fact variables for most soils and aggregates. The presence of amorphous material will also effect this procedure, as shown in Figure 7 on page 19, Appendix II. However, the extent of this influence on minerals other than gypsum is not known at this time.

As noted by Tatlock (1954, p. 11) in comparing diffraction patterns of whole-rock powders that vary widely in composition, absorption effects usually prevent a direct comparison of peak heights of any given mineral as a function of its weight concentration. Specifically, when a mixture contains both a weak and a strong absorber, peaks of the weakly absorbing component appear weaker and those of the strongly absorbing component stronger, than expected from a linear relationship for each component (Klug and Alexander, 1954, p. 411).

To obtain a reasonable degree of accuracy, some method of correcting for the effects of the factors described above must be applied. The adjustment method of Tatlock (1954, p. 20) can be used only if it is known that only one iron mineral is present. The correction methods that can be applied are too time consuming (and thus too costly) for the routine analysis of soil and aggregate materials at the Materials and Research Laboratory.

CONCLUSION

The results of the work done on this project showed that the procedures and techniques required for successful quantitative analysis by the X-ray diffraction-absorption method are too complex and time consuming to be used for the routine analysis of soil and rock samples in this department. While the method is apparently valid for two-component samples if the mass absorption coefficients of the components are within a narrow range many difficulties would be encountered for soils containing many constituents including iron.

The method of quantifying soils and rocks by using calibration curves is rapid and relatively accurate and this method is currently being used by the Materials and Research Department.

REFERENCES CITED

Klug, H. P., and Alexander, L. E., 1954, X-ray Procedures for Polycrystalline and Amorphous Materials: New York, John Wiley & Sons, Inc., 716 p.

Tatlock, D. B., 1966, Rapid Modal Analysis of Some Felsic Rocks From Calibrated X-ray Diffraction Patterns: U.S. Geol. Survey Bull. 1209, 41 p.

APPENDIX I

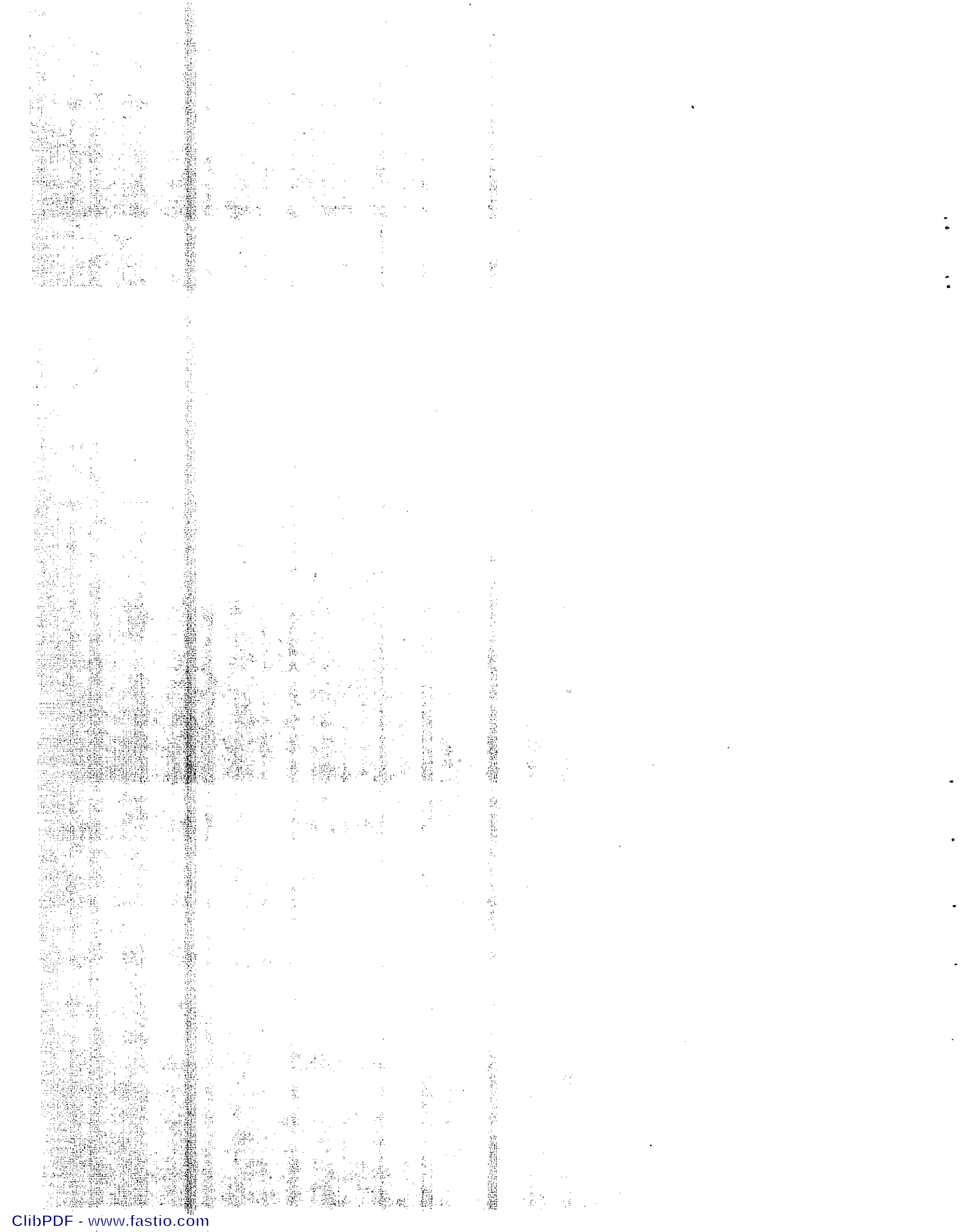


Table 1. - Localities from which the 24 mineral samples were obtained.

Mineral	Number	Location
Kaolin	300-1	Hot Creek, N. of Crowley Lake, Mono Co.
"	300-4	Interpace, Ione, Amador Co.
"	300-10	Cherokee, Butte Co.
"	300-12	Whitmore, Placer Co.
"	300-15	Schoeppe Clay Company, Santiago Creek, Orange Co.
Microcline	400-1	San Diego Cr.
"	400-3	So. Pacific Quarry, Nuevo, Riverside Co.
"	400-5	Campo, San Diego Co.
"	400-6	Kern River near Bodfish, Kern Co.
"	400-7	Near Camptonville, Yuba Co.
Quartz	700-1	Keeler, Inyo Co.
"	700-2	Chili Gulch, Calaveras Co.
"	700-3	So. Pac. Quarry, Nuevo, Riverside Co.
"	700-5	10 Miles NW Yuma, Imperial Co.
"	700-6	1 Mile E. Pine Valley, San Diego Co.
Pyrite	1000-1	Near San Andres, Calaveras Co.
"	1000-3	Mountain Copper Company, Redding, Shasta Co.
"	1000-5	Near Shingle Springs, El Dorado Co.
"	1000-6	Darwin, Inyo Co.
Gypsum	3000-1	American Canyon, Solano Co.
"	3000-2	Between Cantua and Panoche Creeks, Fresno Co
"	3000-3	Fish Creek Mountains, Imperial Co.
"	3000-4	Near Amboy, San Bernardino Co.
"	3000-5	San Gabriel Valley, Los Angeles Co.

Table 2. - Chemical analyses of the mineral samples.

QUARTZ

	700-1	700-2	700-3	700-5	700-6
SiO_2%	98.4	98.6	99.4	99.0	99.2
H_2O (105°C)	Nil	Nil	Nil	Nil	Nil

GYPSUM

	3000-1	3000-2	3000-3	3000-4	3000-5
H_2O (450°F)	19.8	20.1	20.1	18.2	20.0
$CaSO_4$ SO_3 base	77.8	78.6	79.1	73.2	77.7
$CaSO_4$ CaO base (79.6)	1.8	(79.9) 1.3	(79.1)	(80.4) 7.2	(80.1) 2.4
$CaCO_3$	1.3	0.9	Nil	5.3	1.8
SiO_2	Nil	Nil	Nil	2.2	Nil
Total %	98.9	99.6	99.2	98.9	99.5

ORTHOCLASE

	400-1	400-3	400-5	400-6	400-7
SiO_2	64.2	63.0	64.5	64.1	64.4
Al_2O_3	20.4	21.0	19.9	19.6	19.5
CaO	Nil	Nil	Nil	Nil	Nil
MgO	Nil	Nil	Nil	Nil	Nil
K_2O	10.1	12.3	9.2	11.1	12.5
Na_2O	3.4	2.2	3.9	1.9	1.6
H_2O (ign. loss)	*	*	*	*	*
H_2O (105°C)	Nil	Nil	Nil	Nil	Nil
Total %	98.1	98.5	97.5	97.0	98.0

KAOLINITE

	300-1	300-4	300-10	300-12	300-15
SiO_2	60.7	45.9	55.8	46.9	48.3
Al_2O_3	24.5	39.0	26.6	32.0	34.3
CaO	Nil	Nil	Nil	Nil	Nil
MgO	0.3	0.2	0.9	0.6	0.4
Fe_2O_3	Nil	0.2	2.4	4.2	Nil
K_2O	0.4	*	0.8	*	1.6
Na_2O	0.1	*	0.1	*	0.2
H_2O (ign. loss)	11.4	13.6	10.4	15.2	12.7
Total	97.4	98.9	97.0	98.9	97.5

*Test not made.

Table 2.-Chemical analyses of the mineral samples (contd)

PYRITE

	1000-1	1000-3	1000-5	1000-6
S	46.4	38.0	49.0	47.9
SO_4	2.0 (0.7)	3.1(1.0)	*	1.9(0.6)
Fe	43.7	37.6	44.9	42.8
SiO_2	1.8	7.4	1.6	3.6
Al_2O_3	Nil	3.0	*	0.9
CaO	0.2	Nil	*	Nil
MgO	0.7	0.7	*	Nil
CuO	Nil	2.7	*	Nil
FeS_2 based on all S to sulfide	85.5	69.3	91.8	88.6
FeO (OH) based on remaining Fe	4.8	6.7	3.3	1.1
$Fe_2(SO_4)_3$	2.8	4.0	*	2.5
ZnO	*	3.2	*	1.0
TiO_2	1.7	*	*	*
insoluble	*	*	1.4	*
Fe based on S present	39.9(3.8)	32.3(5.3)	42.8(2.1)	41.3(1.5)
Fe based on SO_4 present	0.8(3.0)	1.1(4.2)	*	0.7(0.7)
Total %	97.6	97.4	98.2	97.9

*Test not made.

Number of Counts Required		
Counting error %	Confidence 99.5%	Interval 95%
± 0.25	1,440,000	640,000
0.50	360,000	160,000
1.0	90,000	40,000
2.0	22,500	10,000
3.0	10,000	4,450
4.0	5,625	2,500
5.0	3,600	1,600
10.0	900	400

Table 3. - Count vs. error. A minimum count of 10,000 is used in order that a counting error of 3.0% is obtained at a 99.5% confidence level.

Table 4. - Reproducibility Study

Gypsum Sample 3000-1						
2.88Å, "K" = 15,800*						
	Theoretical			Experimental		
	X	μ_T	X'	μ_T	X''	I(area) (2.88Å)
	.10	13.19	.09	13.61	.09	105
	.20	18.94	.18	19.02	.18	146
	.30	24.70	.33	24.83	.33	211
	.40	30.46	.44	30.26	.44	228
	.50	36.22	.54	36.45	.54	234
	.60	41.96	.66	42.58	.65	246
	.70	47.72	.58	48.67	.56	187
	.80	53.48	.79	54.54	.78	230
	.90	59.23	.95	58.03	.92	246
	1.00	64.99	.93	65.33	.93	225
Mean	.55	39.09	.55	39.33	.54	206
Overall Range			.86		.84	141

X = Actual wt. fraction of gypsum.

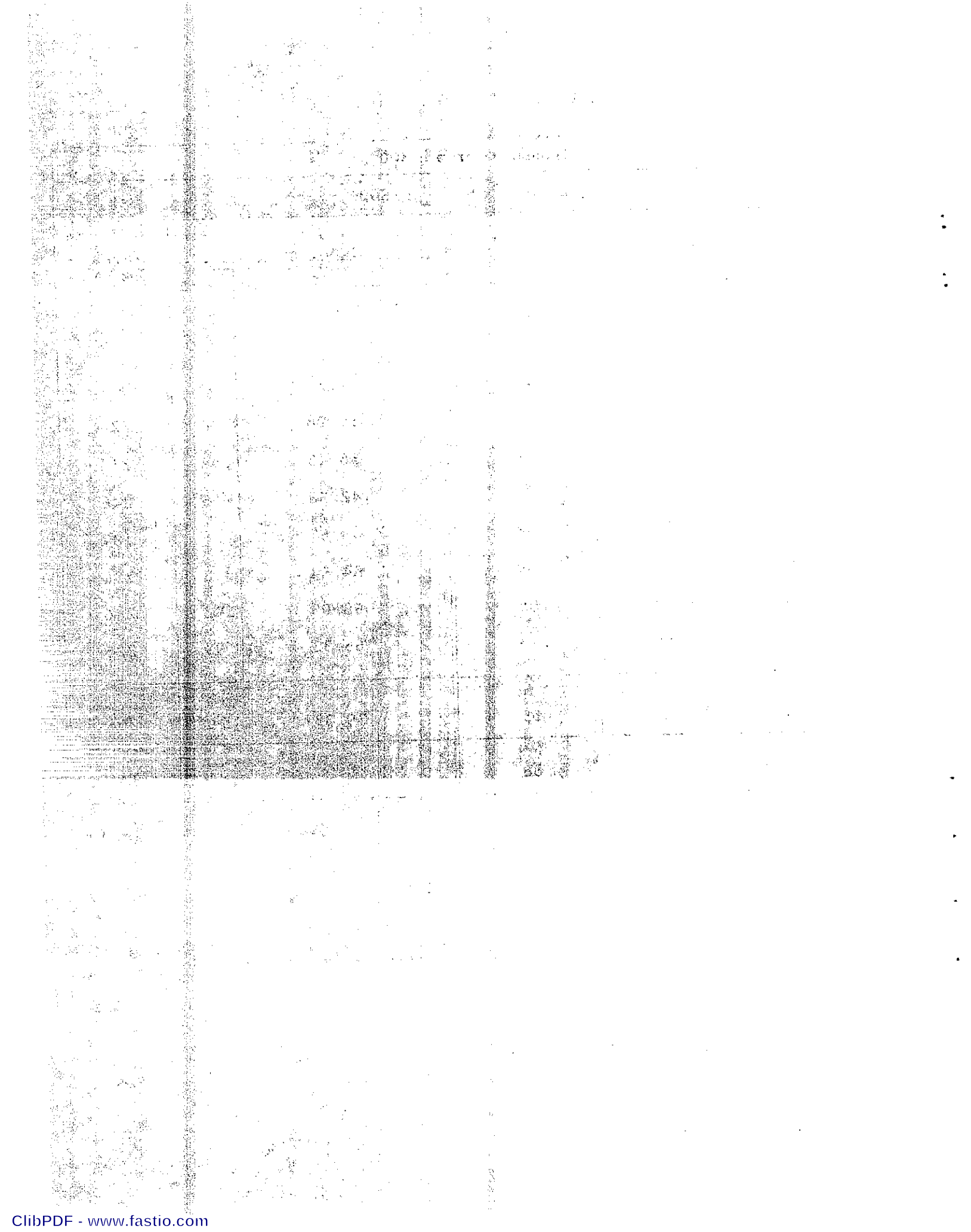
X' = Wt. fraction using theoretical μ_T values.

X'' = " " " experimental μ_T values.

I = Intensity in cps as obtained from the strip chart recorder using the disc-integrator.

* See Figure 4 (a), Appendix I.

$x_i = \frac{Ii}{k} \frac{\mu_T}{}$ (equation 2b).



X-RAY STABILITY

Monochromator, High intensity tube using new Std. 40 data.

Operating procedure:

1. Permaquartz at 26.65° to get I_{max} of the Monochromator.
2. Lif analyzing crystal at 44.94°.
3. No other control.

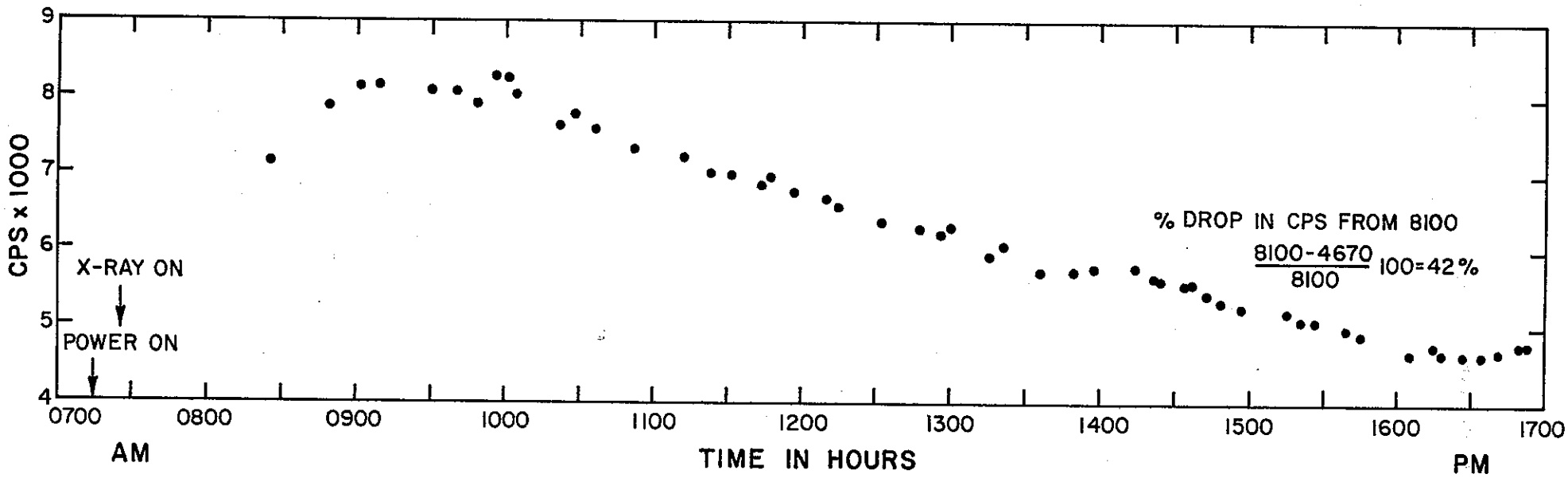


Figure 1

ALUMINUM FOILS VS UNCORRECTED INTENSITY

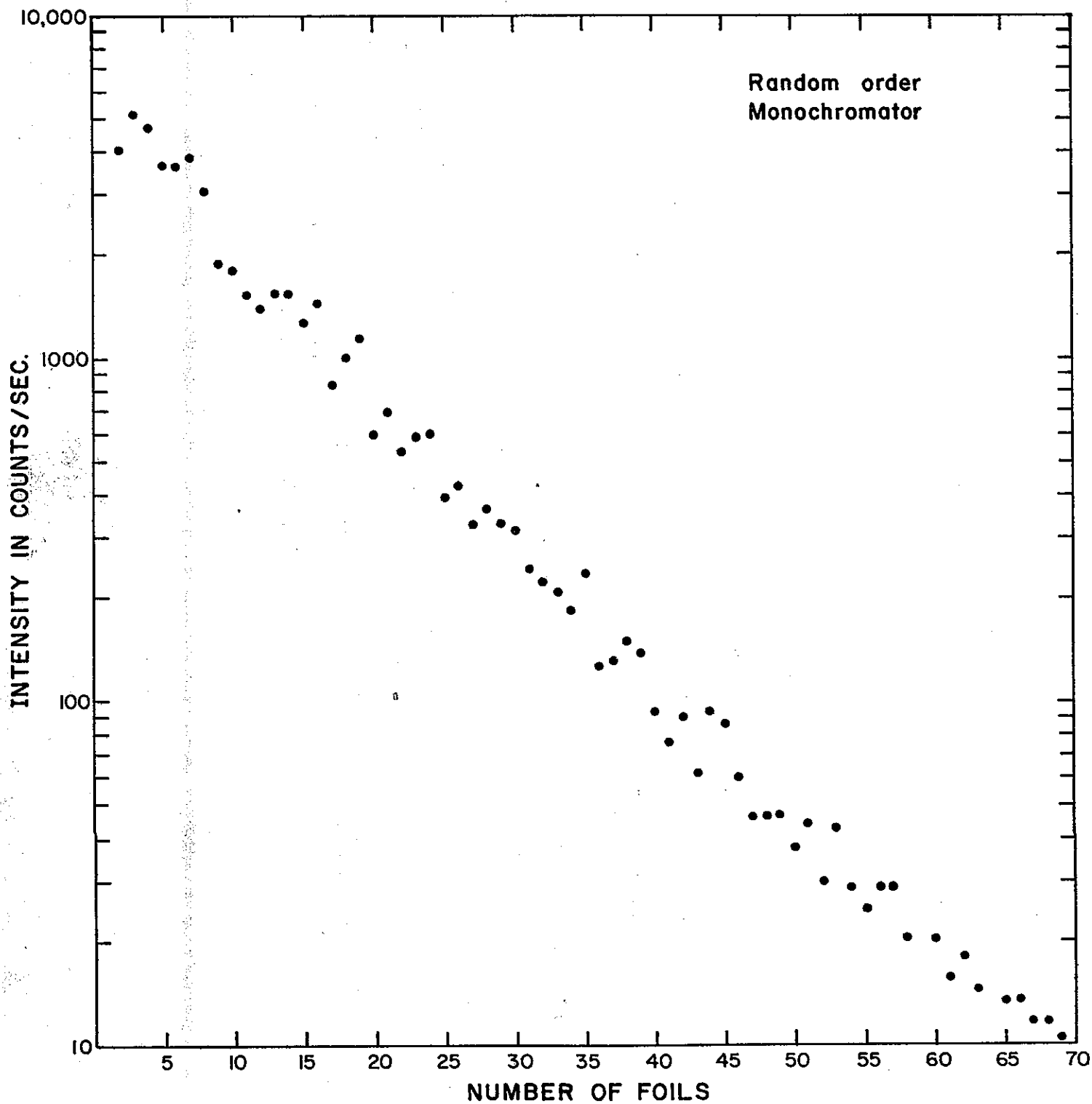


Figure 2

ALUMINUM FOILS VS CORRECTED INTENSITY

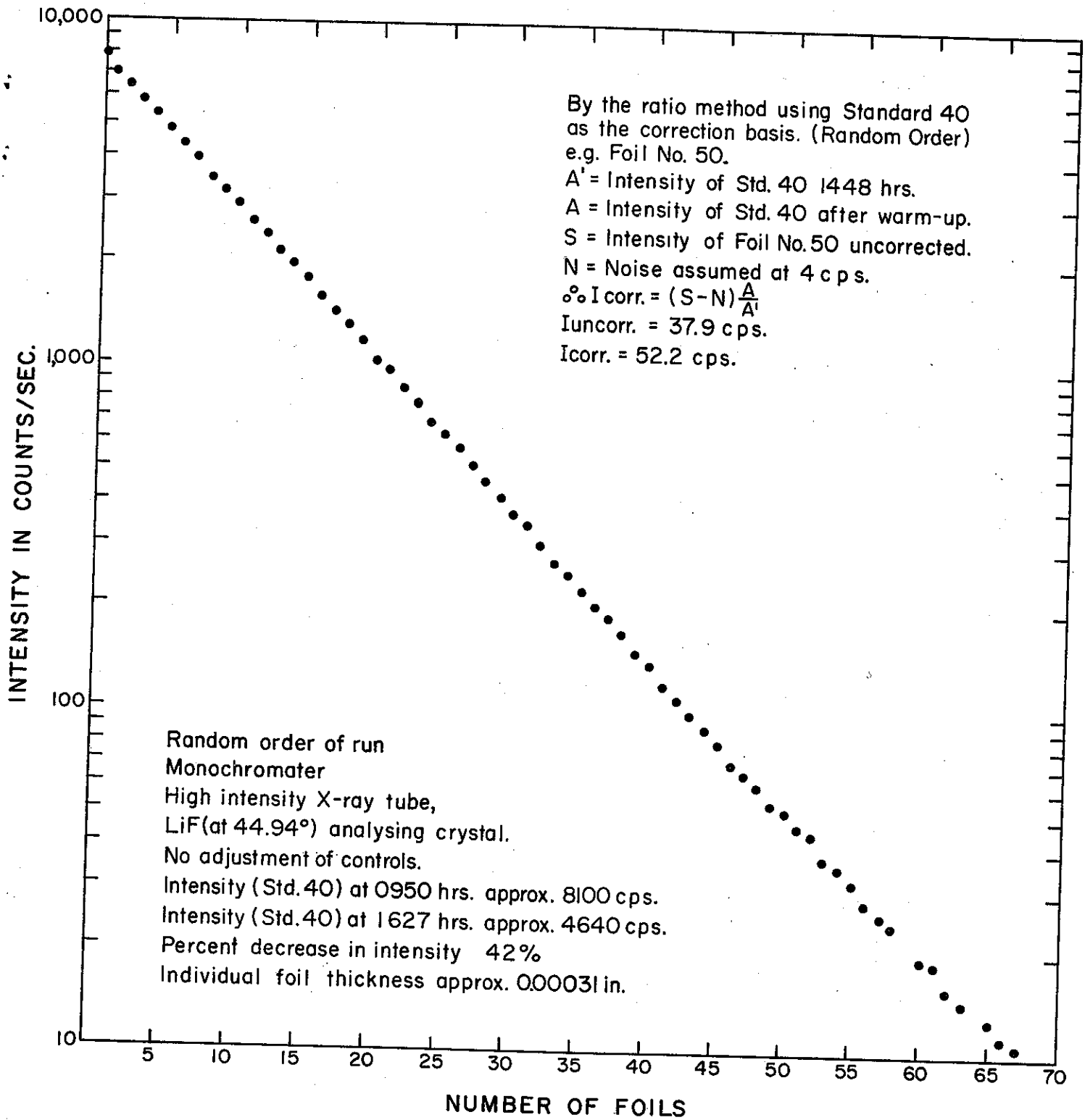


Figure 3

"K" VALUES FOR 50% MIXTURE OF GYPSUM SAMPLE 3000-1

MATRIX = PENTAERYTHRITOL
○ = CALCULATED "K" VALUES
□ = POINTS ON LEAST SQUARES CURVE FIT

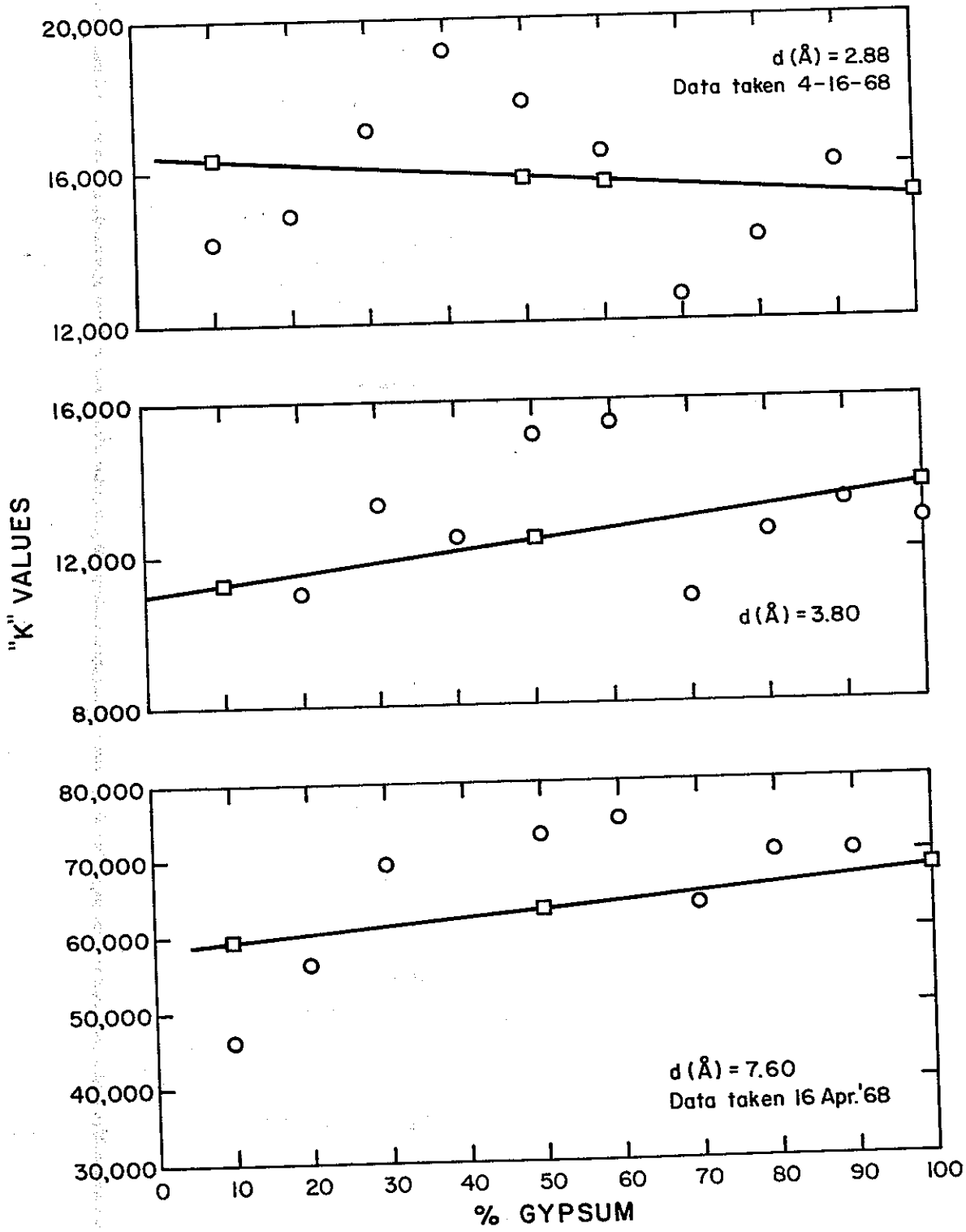


Figure 4

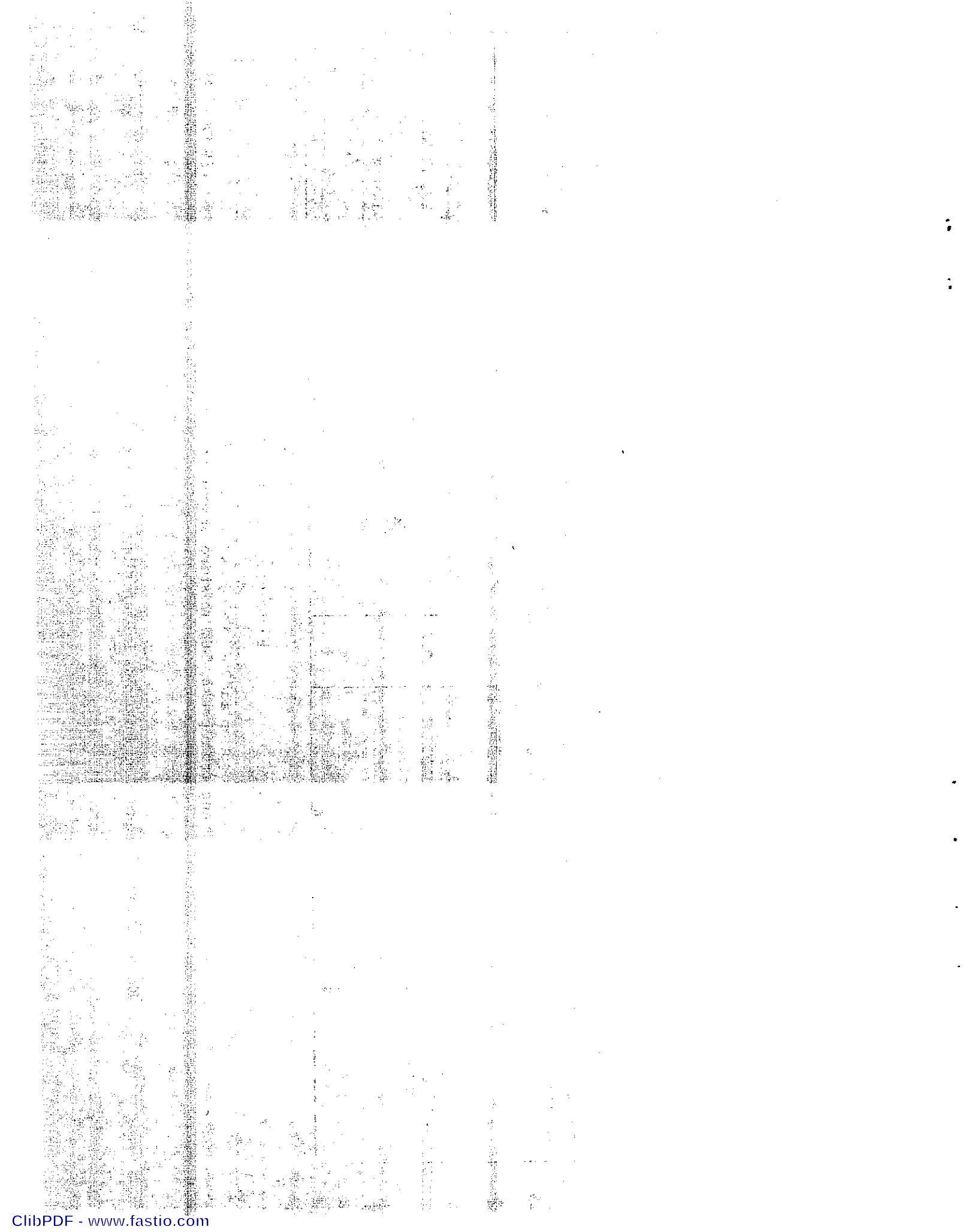
FABRICATION	X-RAY DATA					
Matrix = Pentaerythritol	Noise (CPS)	Standard 50	Sample + Initial Al Foils		Aluminum Foils	
Backpack No. - 34 i^{th} component - Gypsum (3000-1)	7 7 9	19,140 17,254 18,325	CPS 11,105	No. Foils 12	CPS 11,841	No. Foils* 54

CALCULATIONS						
Sample Weight (gross-tare)	ρ, bulk density (I-1.152)	e^x	x	$\mu_T = \frac{x - \mu_{Al}\rho_{Al}(\#)}{\rho_T}$ Mass Absorption	I_i (area)	$k = \frac{I_i \mu_T}{x_i}$
4.5695 - 3.7180 .8515 gm.	.7391	1.0663	.064	.064+4.284=4.348 $\frac{.064-0.102(-42)}{(.1614)\quad .7391}$ $\mu = 36.45$	234 199 961	$k_i = \frac{234(36.45)}{.50}\cdot\frac{18,000}{17,254}=17,796$ $k_i = \frac{199(36.45)}{.50}\cdot\frac{18,000}{17,254}=15,134$ $k_i = \frac{961(36.45)}{.50}\cdot\frac{18,000}{17,254}=73,086$

Figure 5.

Mass absorption and "K" value calculations for the 7.60, 3.80, and 2.88 angstrom peaks, 50% mixture of gypsum, sample 3000-1.

*Equal to sample equivalent foils plus Initial foils, i.e., (12).



APPENDIX II

STATE OF CALIFORNIA—TRANSPORTATION AGENCY RONALD REAGAN, Governor

DEPARTMENT OF PUBLIC WORKS
DIVISION OF HIGHWAYS
MATERIALS AND RESEARCH DEPARTMENT
5900 FOLSOM BLVD., SACRAMENTO 95819

October 1968

Final Report
M&R No. 642992

Mr. J. A. Legarra
State Highway Engineer

Dear Sir:

Submitted herewith is a research report titled:

X-RAY DIFFRACTION TECHNIQUES

TRAVIS W. SMITH
Principal Investigator

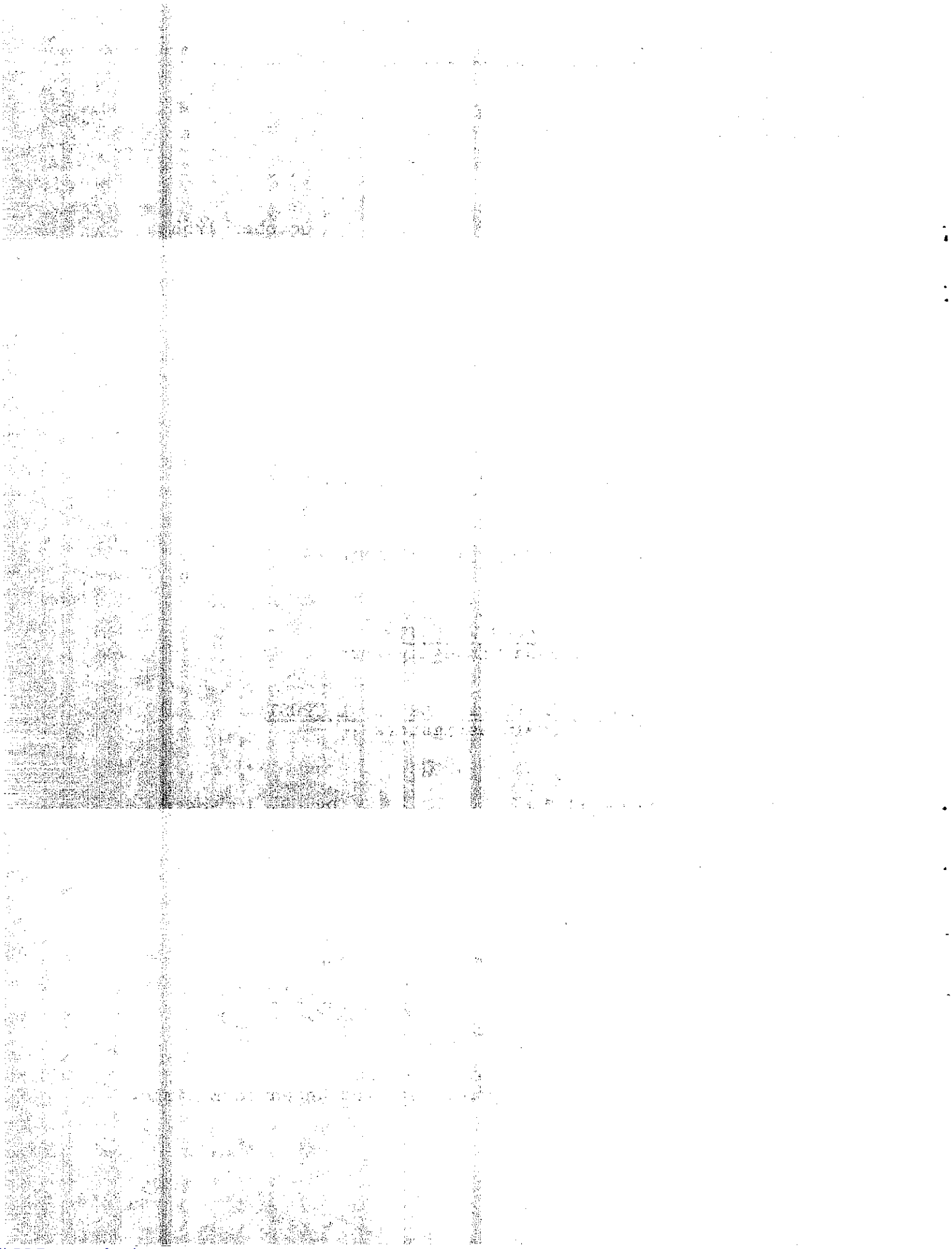
M. L. McCAULEY and DR. J. L. POST
Co-Investigators

Laboratory work by ..... Dr. J. L. Post
J. Gamble

Report prepared by ..... Dr. J. L. Post

Very truly yours,

JOHN L. BEATON
Materials and Research Engineer



REFERENCE: Post, J. L., "X-ray Diffraction Techniques", State of California, Department of Public Works, Division of Highways, Materials and Research Department, Research Report No. 642992, October 1968.

ABSTRACT: Various methods of quantitative analysis and identification of soil minerals by X-ray diffraction were investigated. The study disclosed that the needs of the Materials and Research Laboratory were best met by use of an oriented powder sample in a front pack to identify the non-clay minerals, and by use of strongly oriented coatings on glass slides for clay mineral identification. The slide samples were subjected to two heat treatments (325°C and 550°C), and to glycolation. Most of the clay minerals common in soils were identified by this method and numerous soil aggregates were quantified. The diffractograms of these samples were filed for reference.

The correlation of diffraction peak intensities to the amount of a mineral in an aggregate was studied by using powder samples in which the percent of the constituents was accurately known. A strong diffraction peak, or peaks, characteristic of the mineral was chosen, and the peak heights were plotted against the amount of mineral present. Calibration curves were then drawn from which the amount of mineral present can be determined.

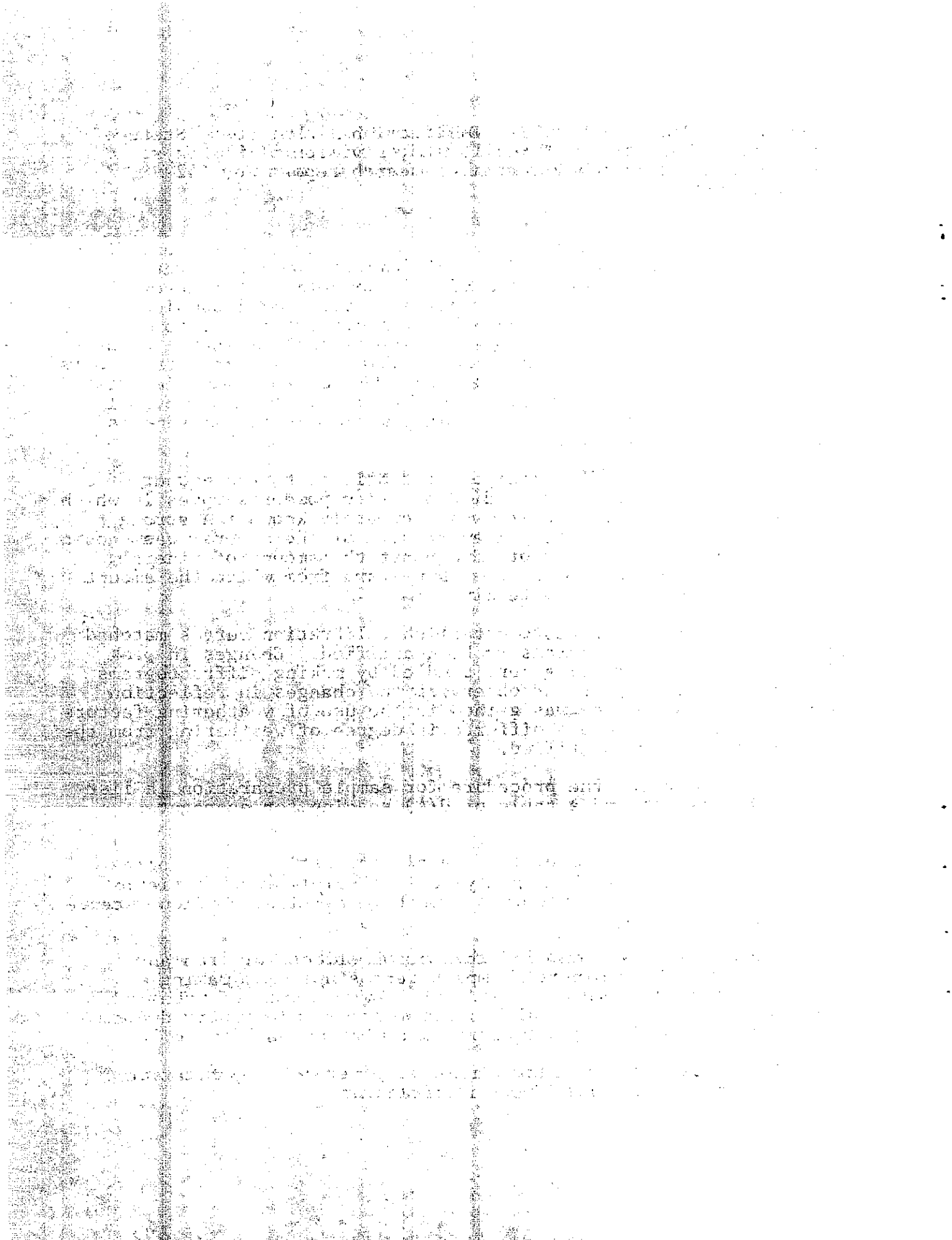
The standard minerals used to establish calibration curves matched the condition of the minerals to be quantified. Changes in peak height caused by weathering were studied by making diffractograms of selected soil samples and observing the changes in reflection intensities. Experience was gained in the use of weathering factors when the standard minerals differed in degree of weathering from the soil minerals being quantified.

A detailed outline of the procedure for sample preparation, a list of auxiliary tests, and a table of d(Å) spacing for aggregate minerals were compiled.

The amount of iron contained in a sample was estimated by making diffractograms of chemically analyzed soil samples with variable iron content. The estimation was made by measuring the flourescence background intensity.

The flourescence background and absorption effects of iron and amorphous material in mineral samples were studied by making diffractograms with samples containing known amounts of iron and amorphous material. The calibration curves were nonlinear due to these absorption effects, but correction charts can be used.

KEY WORDS: Calibrations, clay minerals, minerals, quantitative analysis, samples, soils, X-ray diffraction.



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Introduction

This study was made to evaluate the X-ray diffraction methods of mineral identification and quantitative analysis of soil and rock samples currently used by the Materials and Research Department. Also new procedures and techniques were to be evaluated, to assure that maximum benefit was being obtained from the equipment.

Dr. James L. Post, an Associate Professor of Civil Engineering at Sacramento State College, was retained as a consultant to accomplish the goals of this study. Dr. Post demonstrated for personnel of the Department proper preparation and treatment of samples, the proper use of the equipment and the interpretation of diffractograms. His extensive knowledge of the literature about X-ray diffraction and clay minerals provided many useful references.

As a result of this study, the Engineering Geology Unit is now using an entirely different X-ray diffraction procedure for the identification and quantitative analysis of the mineral composition of soils and rocks.

This research program was completed with the approval and financing of the State of California.

Summary

As a result of this research project, the following procedures have been adopted:

1. A strongly oriented sample is used. This sample is prepared by dense-packing the material using the front-pack method. Clay minerals are identified using two heat treatments (325°C and 550°C) and glycolation of a coating of the sample on a glass slide. This technique provides quick mineral identification and provides a fairly reliable quantitative analysis.

2. Calibration curves showing particular diffraction peak intensities have been developed for use in determining the amount of a mineral present in a sample. The standard mineral used for making the calibration curves must be comparable in terms of crystallinity, chemical composition and degree of weathering to the unknown mineral in the sample. Uniformity in the fabrication of the front-pack samples is essential to obtain consistent results. Precise quantitative analysis of soil mineral aggregate will require auxiliary testing such as differential thermal analysis, microscopic examination or chemical analysis.

3. A systematic method for interpreting X-ray diffractograms was developed, and a list of the more common diffraction peaks was compiled and is included in this report.

4. The goniometer is now being run at 2° 2θ per minute for routine scans and at 0.2° 2θ if greater resolution is required.

5. To increase the resolution, the X-ray tube was turned from line focus to spot focus.

6. The chart recorder was adjusted so that one inch on the graph is equal to 5° 2θ. This permits visual indexing of the graph while the machine is still running.

In addition to developing the above described test procedure, certain other problems were studied. The effect of weathering on crystalline minerals in soil was particularly significant. The effects of iron fluorescence and amorphous minerals on the intensity of background radiation was studied. A method of estimating the amount of iron in a sample based on background intensity is discussed. Non-linearity of calibration curves, caused by X-ray absorption, is possible in certain samples and modification of the method of quantitative analysis based on linear relationships is necessary.

Sample Mounting Procedures

The identification of minerals which comprise rock and soil aggregates may be conducted by X-ray diffraction using two different types of sample preparations. Powder samples with varying degrees of random orientation obtained by one of several different packing procedures are used with the X-ray diffractometer, and a spindle or wedge containing powder samples are used with the X-ray powder camera. Oriented samples, consisting of powder packs or films of air-dried soil slurries on mounts, are used with the X-ray diffractometer and single-crystal mounts are used with the X-ray powder camera.

Quantitative analysis of mineral aggregations may be conducted by the use of oriented samples or samples with some degree of random particle orientation. The mineral analysis is ordinarily conducted in conjunction with supporting physical and chemical tests, such as clay-size content and equivalent iron sesquioxide content.

The degree of accuracy that may be obtained in the quantitative analysis of mineral aggregations by X-ray diffraction, with ordinary supporting tests, is largely dependent on the time available and the experience of the investigator. The mineral aggregation may be investigated as a whole or it may be separated into discrete particle-size ranges, such as the clay-size material. No one method should be adopted in exclusion of the others, rather the method should be used that best suits the degree of accuracy required and the time that is available for each case.

Rapid identification of aggregate minerals may be effected by using a front-pack powder sample and the mineral identification may be facilitated by firmly pressing the powder into the holder so that a strongly preferred orientation is obtained. Most soil minerals, other than quartz, tend to orient readily because of their cleavage characteristics, and because many soil aggregates are rather poorly crystalline the preferred orientation of the powder sample enhances the intensity of the diffraction peaks facilitating the identification and the quantitative analysis of the soil minerals.

The clay mineral suite is most readily identified by the process of preparing oriented coatings of the sample on glass slides and following the procedures given by Warshaw and Roy(1). The identification of small particles of hand-picked minerals from aggregates may usually be made by cementing a cluster of the particles on a glass slide and obtaining a diffraction pattern. Minerals on petrographic slides may be identified in the same manner according to Tatlock(2).

The reliability of quantitative analysis by X-ray diffraction is dependent on the consistency of sample preparation no matter which method of sample preparation is used. The variation in diffraction peak intensities of any mineral is largely dependent on the crystallite orientation and the bulk density of the powder sample, not to mention degree of crystallinity. Pressed pellets made from a powder sample give a preferred orientation to the sample comparable to a pressed front-pack powder sample, however, the sample bulk densities are probably more consistent. One disadvantage of the pressed pellet is the friability of pellets formed from framework silicates.

Random-orientation powder samples may be prepared both by front-pack and back-pack procedures, not to mention glass spindles for powder camera work. Comparable results may be obtained with each method, depending upon the experience and technique of the investigator. The powder sample may require a cover when using a General Electric X-ray diffractometer because the sample holder is placed in an upright position on the goniometer, whereas the Norelco sample holder is held in a horizontal position. A thin sheet of colloidon is sometimes used to cover the front-pack sample.

The back-pack procedure is often used because the method gives quite consistent results, even when used by different investigators. The procedure requires considerable time for the preparation of a randomly-oriented powder sample as does the randomly-oriented front-pack method, perhaps the larger part of an hour per sample in comparison to five minutes for the pressed front-pack method. The back-pack procedure does not give complete random orientation under many conditions of preparation, such as pressure on the back of the sample.

A list of advantages and disadvantages of different packing methods is included to give some idea of the many choices available.

Packing Methods

Front-Pack (pressed)

Advantages:

1. Quick mineral identification and fairly reliable quantitative analyses.
2. Moderate control of orientation (preferred orientation).
3. Intensification of necessary mineral identification peaks.
4. Material passing a No. 200 sieve suffices.

Disadvantages:

1. Some variation in degree of orientation and bulk density.
2. Accuracy of results less than randomly-oriented front-pack.

Back-Pack

Advantages:

1. Fairly consistent packing density.
2. Consistent μ^* values determined by X-ray transmission.

Disadvantages:

1. Irregular degree of orientation (feldspars strongly oriented).
2. Major soil mineral identification peaks suppressed (orientation & lower density).
3. Time-consuming preparation of samples.

Pellet

Advantages:

1. Some control of preferred orientation and density.
2. Quick preparation and mineral identification with fairly consistent peak heights.

Disadvantages:

1. Pellets often friable causing diffraction trace distortion.
2. Surface of material with high $\%\omega$ adheres to compactor.
3. Sorting of mixture when preparing pellet.

Glass Slide (& porous filter method)

Advantages: 1. Strong basal orientation for clay mineral identification.

2. Amenable to quick heat treatment and fairly reliable results.

Disadvantages: 1. Mineral sample thickness and consistency irregular.

2. Only good for clay mineral determinations (water sorting).

Quantitative Analysis Methods

There are two ordinary methods of conducting quantitative analyses of mineral aggregations using an X-ray diffractometer: by determining the area under certain characteristic diffraction peaks, Klug and Alexander (3); by determining the heights of certain diffraction peaks, Tatlock (2); some combination of peak heights and contained areas, Schultz (4). In each case the intensity of diffraction is considered to be directly related to the amount of material present in the aggregation when the random-radiation background is accounted for.

The effect of physical weathering of minerals ordinarily has a far greater effect on diffraction peak intensities than any other factors, see page 422 ref. (3), except perhaps the degree of crystallinity of the aggregation when formed. Because of the number of minerals present in most soils and the physical weathering of the minerals, it is often necessary to depend upon diffraction peak heights for estimating the quantity of each mineral present. The large combination of diffraction peaks obscure one another, the peak heights are reduced by physical weathering, and the true radiation background is difficult to determine.

Diffraction Peak Intensities

The amount of a mineral in an aggregate may be correlated to diffraction peak intensities by several different methods. Ordinarily, a strong diffraction peak, or peaks, characteristic of the mineral is chosen which is not subject to undue interference from other mineral diffraction peaks and the peak height or enclosed area of the peak is related to the amount, by weight, of the mineral present. The calibration curves thus derived are not necessarily linear functions although many soil minerals appear to give linear correlations.

Standard minerals must be chosen which are representative of the minerals contained in the aggregate being investigated because the accuracy of an analysis depends directly on how well the standards are chosen, as indicated by Brindley, p. 501 (5).

The standard minerals may be derived from the aggregate samples or the minerals may be matched by materials from other sources. If other source material is used it must be comparable in terms of degree of crystallinity, chemical composition, and degree of weathering that has occurred.

The method of sample preparation is important because some soil minerals, such as clays and gypsum, are readily altered or destroyed by certain physical treatment such as over heating or over grinding. Powder samples consisting of a crystallite size of about 20μ tend to give best diffraction intensities and, perhaps, random orientation. It is not ordinarily necessary to grind material finer than 74μ (No. 200 sieve) for quantitative approximations if the pressed front-pack is used. A disc pulverizer may be used for an initial grind, followed by dry-grinding of a split-out sample by mortar and pestle.

General Procedure

After the sample is received the following preliminary treatment should be done:

1. Air dry the sample and break down weakly cemented particles with rubber pestle.

2. (a) Coarse Aggregate - Split out representative portion and reduce material to particles passing a No. 40 sieve using a disc pulverizer.

   (b) Fine Aggregate (soils) - Split out representative portion and separate the material passing the No. 10 sieve, weigh the material larger than 2 mm, and treat the larger material the same as the coarse aggregate if it comprises more than 10-15% of the total aggregate.

3. Determine the clay-size content of material passing the No. 10 sieve by the hydrometer analysis method. Clay-size material may be separated from the sample at this time as required. A cyclone separator may also be used.

4. Split out a portion, about 10-15 gms, of pulverized aggregate or soil and grind the material with a ceramic mortar and pestle. Reduce the aggregate and sandy or silty soil to material passing a No. 200 sieve (74μ) and reduce clayey soils to material passing a No. 140 sieve (0.1 mm). If clay-size material is separated from the sample it should be reduced to powder for mixing and handling purposes.

5. Put the reduced samples in sealed containers and mix thoroughly for further use.

6. Prepare samples of coarse-grind and soil aggregations for auxiliary physical-chemical tests (20-25 gms) where necessary.

Auxiliary Tests

It is seldom possible to conduct a very precise quantitative analysis of soil mineral aggregates without auxiliary tests. The tests required for different soils must be judged by the investigator. The tests may include:

1. Total carbonate content by gravimetric determination.
2. Total organic mineral content by heating or peroxide method.
3. Water-soluble content by leaching method.
4. Clay-size content by hydrometer analysis.
5. Ferric iron content by iodometric titration method or X-ray fluorescence background measurements.
6. Gypsum content by weight loss from dehydration (50° - 100°C).
7. Differential thermal analysis of clay minerals.
8. Heat treatments and "Glycolation" of oriented slides of clay minerals.
9. Optical investigation of coarse aggregates.
10. Specific chemical analyses such as Na^+ cation content.

Less precise quantitative analyses of soils may be made by grinding a representative portion of the total air-dry sample with a disc pulverizer, splitting the coarse-grind material, and preparing a powder sample in the same manner as with soil fines. In any case, the moisture content of the air-dry soil sample (-#10 size) is required, the oven-dry temperature not to exceed 50°C.

X-ray Diffractogram Analysis

It is convenient to make the diffractogram so that one inch on the chart paper is equal to 5°2θ because sufficiently precise 2θ values may then be derived by visual estimate. The goniometer probably should not be run faster than 2°2θ per minute because the recorder does not have a sufficiently rapid response to keep up with a rapidly varying signal input. Tatlock (2) considers a 2°2θ, drive rate to give results nearly comparable to 1°2θ, which is more commonly used for precise mineral analysis. Use machine recorder constants of 500 CPS, TC = 2, with the G.E. XRD-5 unit.

The diffractogram should be precisely labelled while it is being made and the diffraction 2θ angles and matching "d" spacings may be marked on the chart at that time if convenient. For a complete mineral identification all real peaks above the radiation background should be marked. For quantitative analysis only certain diffraction peaks will be used. A list of the more common diffraction peaks which indicate the presence of different aggregate minerals is given in Table 1, the peaks commonly used for quantitative analysis being marked by an asterisk.

The identification of the aggregate minerals is done in the following manner (3° - 63° 2θ):

1. The quartz peaks are marked. Often 6 of the 10 more prominent peaks are visible. When less than 10 percent quartz is present only 2 peaks may show, 4.26Å and 3.343Å. The 3.343Å quartz peak will often appear when as little as 3 percent quartz is present.

2. The feldspar peaks are marked. When more than about 10 percent feldspar is present it is necessary to make a second scan from 26.0° - 29.0°2θ at 2000 CPS, TC = 1, with a goniometer drive rate of 0.2° or 0.4°2θ per minute, to identify the predominant feldspars so that the feldspar peaks may be properly identified. The 040 diffraction peaks are the main sources of feldspar identification.

3. The amphibole and pyroxene peaks are marked. The most common amphibole is hornblende with primary identification peaks at 8.4Å and 3.12Å. Several of the amphiboles, constituting a solid state series, have primary peaks near 8.4Å 'd' spacing. The most common pyroxene is augite with primary identification peaks near 2.99Å, 2.94Å, and 1.62Å. Augite chemical composition is also variable.

4. The carbonate and sulfate peaks are marked. The primary identification peaks for the carbonates are: Calcite 3.03Å; Dolomite, 2.89Å; and Magnesite, 2.74Å. Aragonite is metastable in soils and not too common. The only common sulfate, gypsum, has a primary identification peak at 7.56Å, but may exist as hemihydrate in dessicated soil. Anhydrite is not common in soils nor is γ $CaSO_4$, the latter being found in gypsiferous soils oven-dried at 110°C, Deer, et al, vol. 5, p. 207 (6).

5. The mica, chlorite, and serpentine peaks are marked. The main diffraction peak for micas occurs at 10.0Å, chlorites at 7.0-7.2Å, and serpentines at 7.36Å. In soils these minerals may be identified along with the clay mineral suite.

6. The less common non-clay mineral peaks are marked. The main diffraction peaks which suggest the presence of these minerals are given in Table 1. If any of these minerals are believed to be present the entire diffraction pattern listing should be checked for those minerals. Halite, magnetite, goethite, zeolites, and cristobalite often occur as minor soil components (< 5%).

7. The clay mineral peaks are marked. The known clay mineral peaks on the powder sample diffractogram are marked and the oriented slide technique is used generally according to the procedure of Warshaw and Roy (1) to identify the clay minerals.

The relative intensities given for X-ray diffraction patterns for different minerals by ASTM Powder Diffraction File and other sources of information are supposed to be for randomly oriented powder samples. The intensity values may be used as a rough guide in mineral identification but diffraction peak intensities obtained in the laboratory are commonly quite different, depending upon the cleavage habits of the minerals and the degree of preferred orientation achieved. Of course, the crystallite size and degree of crystallinity may cause some variations in peak intensities.

Ordinarily powder sample scans are made from 3° to 63° 2θ and oriented slide scans are made from 3° to 21° 2θ at 500 CPS, TC = 2. If it is necessary to identify very poorly crystalline clays a count of 200 CPS may be used. Medium resolution Soller slits are normally used but the high-resolution slits with the 0.05° receiver slit, better resolve the feldspar peaks from 26° to 29° 2θ at 2000 CPS, TC = 1 using a goniometer drive rate of 0.2° 2θ per minute. Much better peak resolution may be obtained by turning the X-ray tube to center port for 'spot' focus and using a 0.05° receiver slit, as shown in Figure 1.

Calibration Curves

Calibration curves may be made for crystalline aggregate minerals by relating selected diffraction-peak intensities to the amount of each mineral present in the aggregate. Calibration curves are derived by mixing together known amounts of soil minerals, or by using previously analyzed mixtures, and making diffractograms of the mineral calibration peaks. The peak heights are then plotted against the amount of mineral present. In some cases the areas under the diffraction peaks are used for quantitative analysis of different minerals. Diffraction peaks commonly used to make calibration curves are marked with asterisks in Table 1.

Quartz is the only major crystalline constituent of rock and soil aggregates that has very poor cleavage, thus, the powder crystallite orientation is quite variable when using a pressed powder sample. By using four calibration peaks for quartz, as shown in Figure 2, and taking the average value a close approximation of quartz content (by weight) may be obtained. The four calibration curves may be considered linear and represent approximately a random powder orientation. Curves representing relatively unweathered quartz may be derived by using diffraction intensity data obtained with a permaquartz slab, the peak heights being plotted as 100% quartz as shown in Figure 2.

Calibration curves for three common aggregate minerals, muscovite, hornblende, and serpentine, are given in Figure 3. The powder samples which were prepared consisted of relatively unweathered material, the muscovite occurring as phyllite, the hornblende as finely crystalline rock, and the serpentine as antigorite. All three of the minerals orient readily and thus

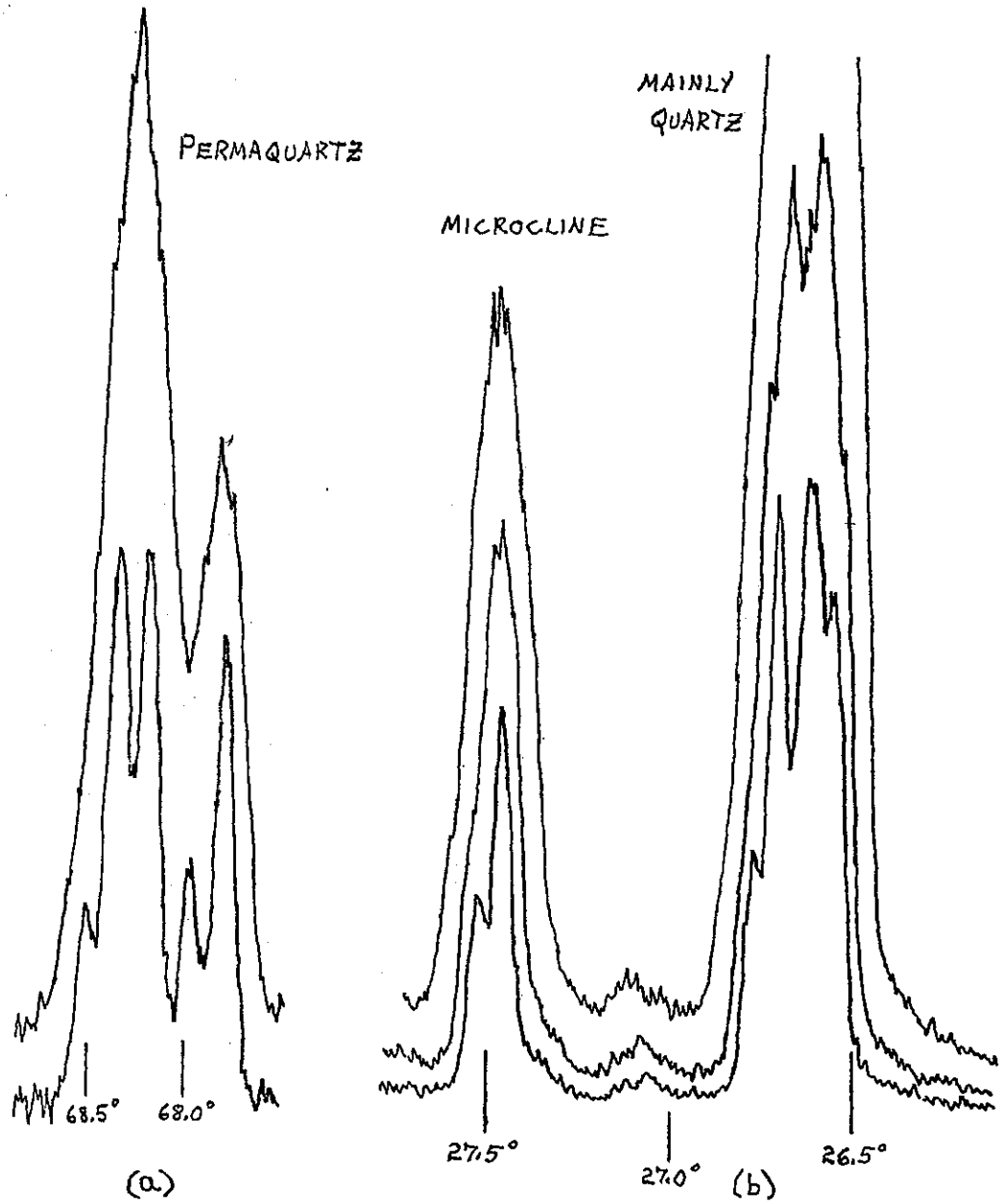

Figure 1. Effect of x-ray tube orientation and resolution slits on diffraction peak intensity and resolution. (a) outer peaks: line source, 200 CPS; inner peaks: spot source, 500 CPS. 0.05° receiver slit. (b) outer peaks: 0.2° slit, middle peaks: 0.1° slit, inner peak: 0.05° receiver slit. Spot source.

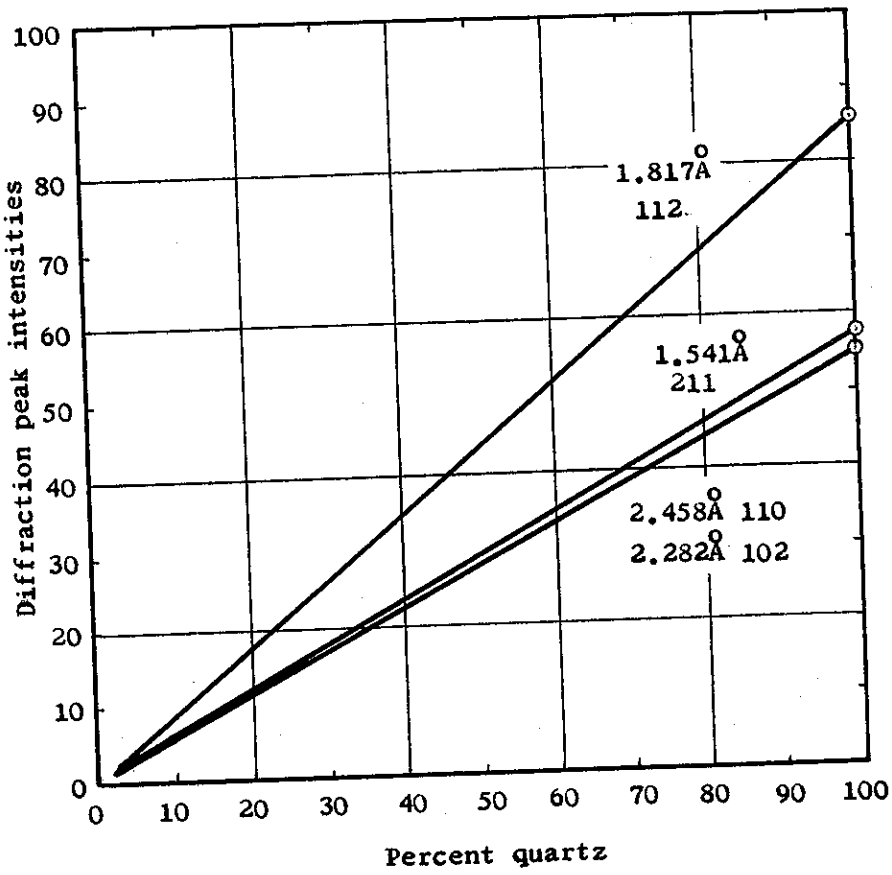

Figure 2. Relationship between quartz content and four diffraction peak intensities, using permaquartz. (G. E. SPG-3 receiver, Cu/Ni, 500 CPS, TC 2, slits: 1^{o}-.2^{o} mr)

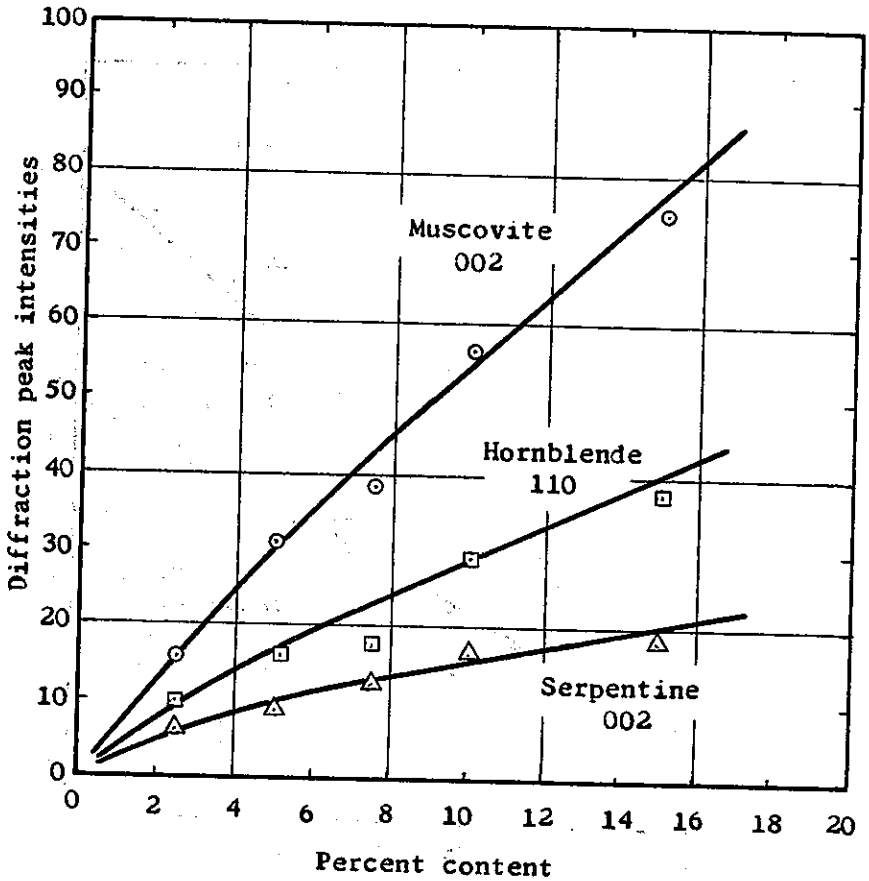

Figure 3. Relationship between mineral contents, muscovite, hornblende, serpentine, and their diffraction peak intensities. (G. E. SPG-3 receiver, Cu/Ni, 500 CPS, TC 2, slits: 1^{o}-.2^{o} mr)

give quite reliable results when using the pressed-powder packing technique.

The feldspars usually occur as perthite, a sodic plagioclase in microcline, and require special treatment for detailed identification. Feldspars possess perfect cleavage and the powder crystallites tend to orient so that the 0k0 diffraction peaks are enhanced. Calibration curves may be made using feldspar 040 diffraction-peak intensity measurements. Because of the intensity of the diffraction peaks and the close spacings of the feldspar 040 peaks, it is necessary to scan at a slow rate (0.2° 2θ minute) and to change count rate from 500 CPS to 2000 CPS when more than about 10 percent feldspar is present. Figure 4 shows a typical calibration curve for total feldspar content (Σ 040 peak heights).

The standard minerals which are used to establish calibration curves must match the condition of the minerals which are to be quantified, especially with respect to degree of crystallinity and chemical composition. If the minerals in the aggregate only vary from the standard minerals in the degree of physical weathering, the most common situation, a weathering factor must be introduced or additional standard minerals must be secured from the aggregate or its equivalent. When many rock and soil aggregates with varying degrees of physical weathering are to be considered it is necessary to establish weathering factors to account for the decline in intensity of the mineral diffraction peaks.

Soil and rock minerals vary in their resistance to physical and chemical weathering so that each mineral will have a distinct weathering range. Some minerals are very stable and show little effect from weathering. Quartz, for example, shows a peak diffraction intensity for dune sand or extremely weathered tropical soil that is about two-thirds that of unweathered material. Chalcedony (cryptocrystalline α-quartz) shows about the same peak intensity as extremely weathered quartz. A maximum weathering factor (multiplier) of 1.50 might be used for quartz to adjust to standard calibration curves for unweathered quartz, and, of course, there are also degrees of weathering to consider.

Most soil and rock aggregates are crystalline, excepting unweathered igneous extrusives which contain glassy material, and because of this crystallinity the sum of the minerals, represented by diffraction peaks, must total nearly 100 percent when including organic material and water content. Knowing the rate and degree of weathering possible for different minerals a reasonable estimate of the aggregate mineral content may be made. Some soil minerals are very subject to chemical weathering and do not appear to require weathering factors, including amphiboles, pyroxenes, and serpentines. Either they are present as formed or they are chemically altered. Calibration curves for authigenic soil minerals, such as sedimentary chlorite, must be derived partly from allied tests. As an example,

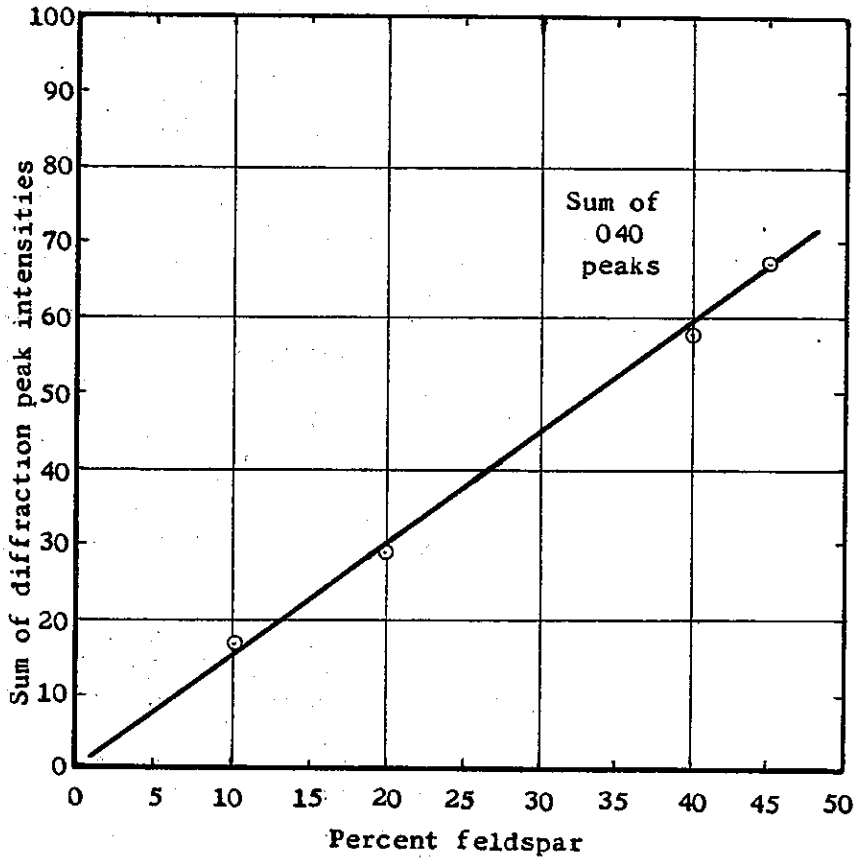

Figure 4. Relationship between feldspar content and 040 diffraction peak intensities. (G. E. SPG-3 receiver, Cu/Ni, 2000 CPS, TC 1, slits: 1^{o}-.1^{o} mr)

certain extremely weathered tropical soils were found to consist of only quartz and kaolinite with a trace of goethite, Post (7). The hydrometer analysis established the clay-size content (kaolinite) and the equivalent ferric iron content was found chemically (giving goethite), the remaining mineral then being quartz. By deliberately choosing simple two, three, or four-mineral systems the weathering stage of aggregates of an area may thus be determined.

Some comparison of the effect of weathering on different minerals may be shown by considering perthite in relation to quartz. Where extremely weathered quartz may require a weathering factor of 1.5, extremely weathered perthite in rock may require a factor of 2 and in soil a factor of 3. Whereas micas are very stable minerals in aggregates with little change in crystallinity from physical weathering, clay minerals such as kaolinite and montmorillonite may appear to be nearly amorphous after extreme physical weathering. Illite (hydromica) is ordinarily considered to be formed by the chemical weathering of micas, part of the K^+ ions being removed from the interlayer position. The K^+ ions are weakly bonded, being held in 12-fold coordination by the silica Tetrahedra. Illite and kaolinite in soil aggregates ordinarily show about the same diffraction intensities for first order (001) basal spacings.

Diffraction Analysis Problems

Under certain conditions the total iron in soil and rock aggregates may be estimated by measuring the fluorescence background intensity on the diffractogram, Figure 5, and when the iron is known to be contained in one mineral the amount of mineral contained may also be estimated, as shown by Tatlock (2). Several common aggregate minerals contain variable amounts of iron, including hornblende, augite, and biotite, and many soils also include clay minerals which contain iron. The common soil mineral goethite, $Fe_2O_3 \cdot H_2O$, is not very susceptible to X-ray diffraction and ordinarily must be quantified by chemical analysis. The weakness of the X-ray reflections are presumably due to fine grain size rather than poor structural order, Weaver, et al (8). It may be seen, Figure 5, that the background caused by goethite appears to include not only radiation scatter caused by iron fluorescence but also scatter caused by the microcrystalline nature of goethite, and possibly by the presence of amorphous material.

Iron is the only relatively abundant common rock-forming element whose fluorescence under copper radiation effects appreciable increases in background radiation. Not only does the fluorescence background caused by iron tend to cover other mineral diffraction peaks, Figure 6, but because iron is a strong radiation absorber ($\mu^* = 324$), peaks of the weakly absorbing component appear weaker and those of the strongly absorbing component appear stronger, Klug and Alexander (3).

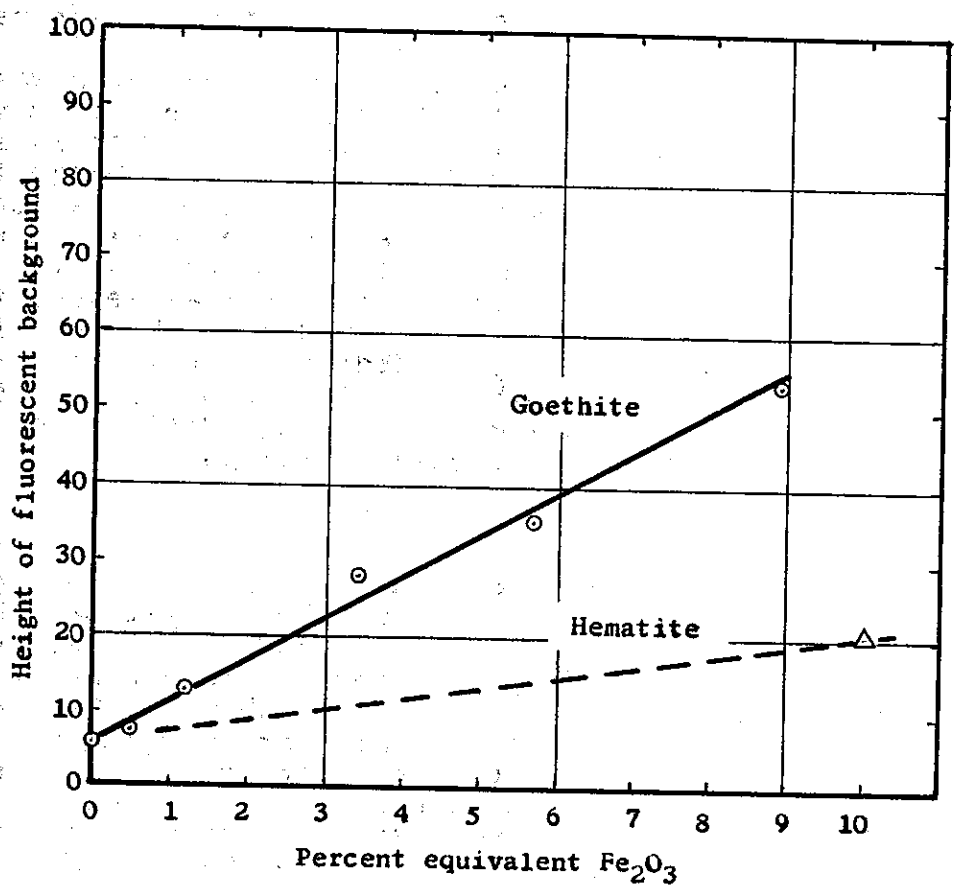

Figure 5. Fluorescent background on diffractogram due to iron content of aggregate mineral sample, 15° - 20° 2θ. (Gas flow counter, 500 CPS, TC 2)

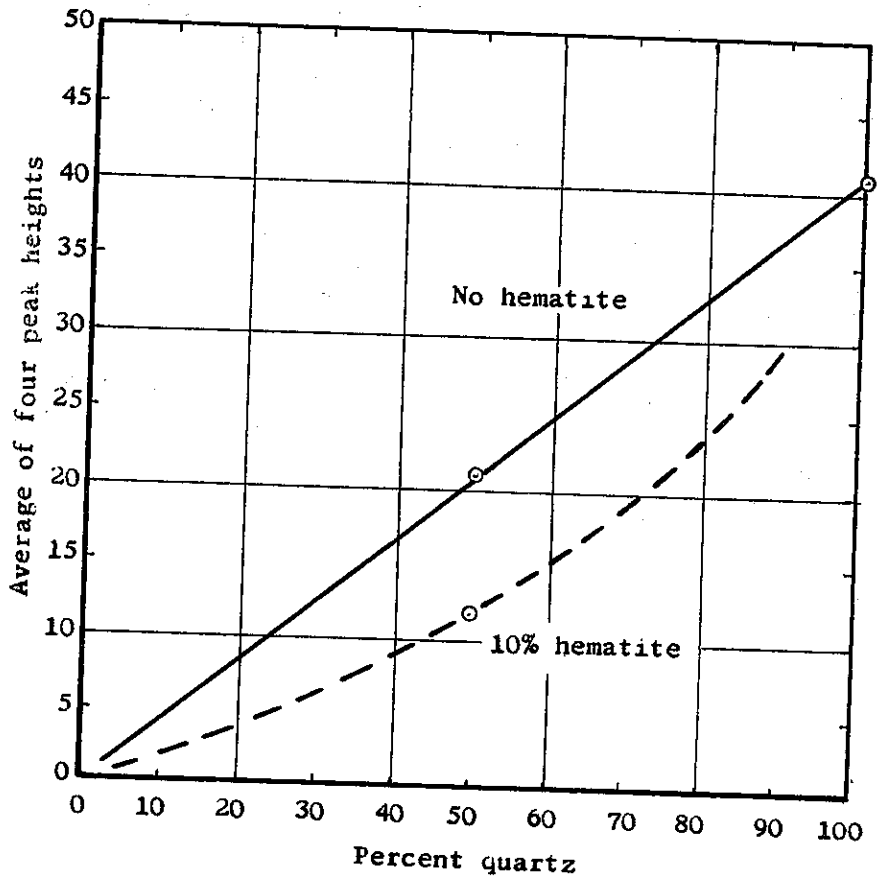

Figure 6. Effect of hematite on four diffraction peak intensities, sum of quartz 110, 102, 112, and 211 reflections. (Gas flow counter. 500 CPS, TC 2)

The effects of iron in the X-ray diffraction analysis of aggregates may be adjusted by the use of correction charts as Tatlock (2) has proposed or the effects of iron may be negated by using an iron or chromium X-ray tube target. Unfortunately, the iron and chromium X-ray tubes do not give as useful diffraction patterns as the copper tube.

Amorphous minerals raise the diffraction background intensity in varying amounts, probably in some relationship to the mass absorption coefficient of the amorphous material present. Silicic acid, $SiO_2 \cdot nH_2O$, gives a very low background intensity ($\mu^* = 29.7$) whereas micro-crystalline goethite gives a very high intensity ($\mu^* = 208.5$).

In comparing diffraction patterns of aggregate powders, absorption effects are present that cause calibration curves to be non-linear. Whenever mass absorption coefficients of any two predominant aggregate minerals vary considerably the calibration curves may appear as shown in Figure 7. This does not hinder the use of the analysis procedure but it must be remembered that the linear relationship given by Klug and Alexander (3) may not be used without some modification.

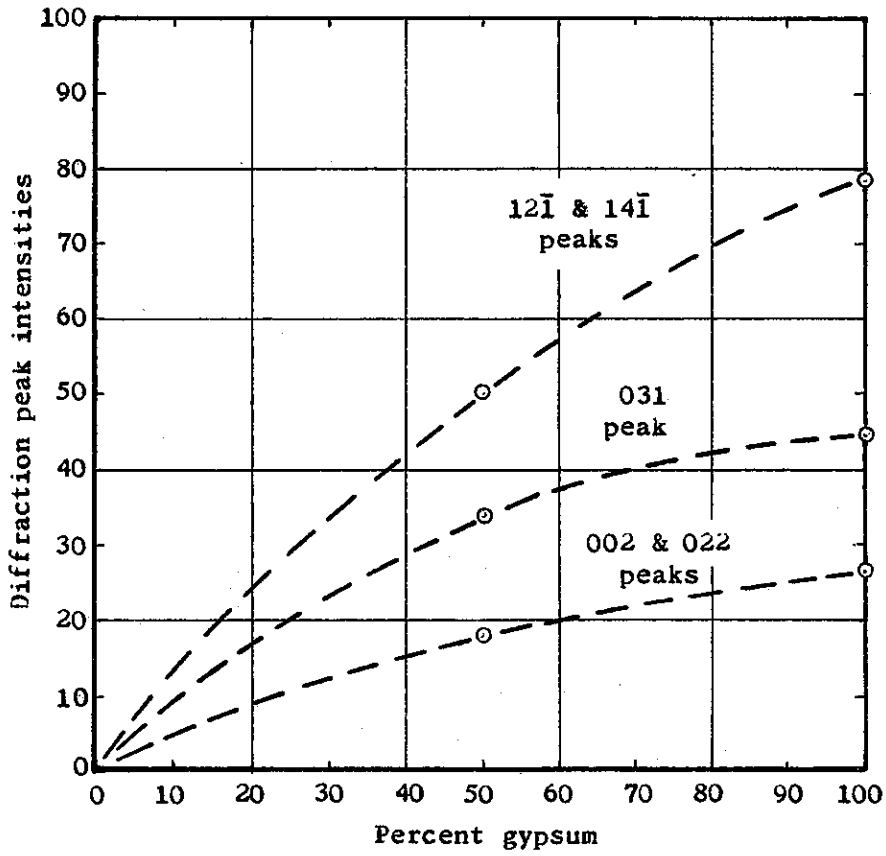

Figure 7. Effect of amorphous silicic acid, $SiO_2 \cdot nH_2O$, on diffraction peak intensities of gypsum. (Gas flow counter, 500 CPS, TC 2)

REFERENCES

1. Warshaw, C. M., and Roy, R. "Classification and a Scheme for the Identification of Layer Silicates," Geol. Soc. of America Bulletin, Vol. 72, No. 10, Oct. 1961, p. 1455-1492.

2. Tatlock, D. B. "Rapid Modal Analysis of Some Felsic Rocks from Calibrated X-ray Diffraction Patterns," Geol. Survey Bulletin 1209, Wash., D.C., 1966.

3. Klug, H. P., and Alexander, L. E. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, John Wiley and Sons, Inc., N.Y., 1954, p. 410-438.

4. Schultz, L. G. "Quantitative Interpretation of Mineralogical Composition from X-ray and Chemical Data for the Pierre Shale," Geological Survey Prof. Paper 391-C., Wash., D.C., 1964.

5. Brown, G. (ed) The X-ray Identification and Crystal Structures of Clay Minerals, Mineralogical Society, London, 1961, p. 489-514.

6. Deer, W. A., Howie, R. A., and Zussman, J. Rock-Forming Minerals, Vols. 1-5, John Wiley and Sons, Inc., N.Y., 1962.

7. Post, J. L. Engineering Characteristics of Some Southeast Asian Soils, Technical Report No. AFWL-TR-67-143, Air Force Weapons Laboratory, Kirtland AFB, New Mexico, May 1968.

8. Weaver, C. E., Wampler, J. M., and Pecuil, T. E. "Mossbauer Analysis of Iron in Clay Minerals," Science, Vol. 156, April 1967, p. 504-508.

APPENDIX

d(Å)Spacings for Aggregate Minerals

Calibration Diffractograms

Table 1

d (Å) Spacings for Aggregate Minerals

	d(Å)	I	Mineral	Notes
*	15.0-12.5	vs	Mont. Group (Smectite)	varying degrees of hydration
	14.5-13.5	vs	Chlorite	
*	14.5-13.5	vs	Vermiculite	fully hydrated
*	12.5-12.0	vs	Vermiculite	partially hydrated
*	10.5	vs	Attapulgite	(palygorskite)
*	10.1	s	Illite	
*	10.1-9.9	vvs	Micas	muscovite, biotite, phlogopite
*	9.3	s	Talc	
*	8.5-8.4	vs	Amphibole	hornblende, actinolite
*	7.56	vs	Gypsum	
*	7.36	vs	Serpentine	antigorite, chrysotile
*	7.5-7.2	mw	Halloysite	metahalloysite ($2H_2O$)
*	7.15	s	Kaolinite	
*	7.2-7.0	vs	Chlorite	iron-rich chlorites to 6.78Å
	6.65	m	Orthoclase	"high" K-feldspar
	6.46	m	Microcline	"low" K-feldspar
	6.55-6.38	m	Plagioclase	anorthite to albite
*	5.61-5.57	mw	Analcite	
*	4.85	s	Gibbsite	
	4.79-4.69	ms	Chlorite	
*	4.50-4.45	m	Clay 020-040	mainly kaolinite & smectites
	4.37	m	Gibbsite	
	4.27	s	Gypsum	
	4.26	s	Quartz	and K-feldspar 4.24-4.21Å

(* Peaks used for quantitative analysis)

	d(Å)	I	Mineral	Notes
*	4.18	vs	Goethite	
*	4.04	vs	Cristobalite	and plagioclase peak
	4.04-4.02	mw	Plagioclase	albite to anorthite
	3.97-3.84	mw	Feldspars	
	3.83-3.79	s	K-feldspar	microcline & orthoclase
	3.77-3.74	ms	Plagioclase	
	3.66-3.61	ms	Plagioclase	
	3.66-3.64	s	Serpentine	
	3.57	ms	Kaolinite	
	3.59-3.52	s	Chlorite	
	3.48-3.46	m	Feldspars	
	3.43	s	Analcite	
	3.37-3.36	vvs	Micas	muscovite and biotite
	3.343	vvs	Quartz	
	3.33	vs	Orthoclase	
*	3.245-3.225	vvs	Microcline	and orthoclase
*	3.21-3.19	vvs	Plagioclase	albite to anorthite
	3.18	vvs	Plagioclase	only albite and oligoclase
	3.17-3.16	s	Plagioclase	only andesine to anorthite
	3.13-3.11	wm	Plagioclase	only andesine to anorthite
	3.13-3.09	s	Amphibole	hornblende and actinolite
	3.10	vs	Talc	
	3.09	vs	Jarosite	
	3.06	s	Gypsum	
*	3.03-3.02	vvs	Calcite	
	3.01	vs	Alunite	

	d(Å)	I	Mineral	Notes
	3.01-2.95	ms	Feldspars	131 Peak
	2.99	s	Augite	
	2.94-2.91	mw	Feldspars	
*	2.89	vs	Dolomite	
	3.87-2.82	mw	Chlorite	
	2.86-2.82	mw	Feldspars	131 peak
	2.82	vs	Halite	
	2.75	s	Ilmenite	
	2.74	vs	Magnesite	
	2.71-2.69	s	Amphibole	hornblende & actinolite
	2.69	sb	Hematite	and goethite
	2.56	s	Augite	
	2.56-2.51	m	Feldspars	and micas
	2.53	s	Magnetite	
	2.51	s	Augite	and hematite
	2.50-2.44	mw	Feldspars	albite to labradorite
	2.48	m	Cristobalite	
*	2.458	mw	Quartz	
	2.33	m	Kaolinite	
*	2.282	mw	Quartz	and calcite
	2.19	ms	Dolomite	
	2.10	mw	Calcite	
	2.01-1.99	m	Micas	muscovite & biotite
	1.99	s	Halite	
	1.91	mw	Calcite	
	1.87	mw	Calcite	

	d(Å)	I	Mineral	Notes
*	1.817	mw	Quartz	and dolomite
	1.82-1.80	mw	Feldspars	
	1.78	mwb	Dolomite	
	1.62	mw	Magnetite	
	1.56	ms	Septichlorites	esp. Chamosite (060)
	1.55-1.53	w	Chlorites	060 peak
*	1.541	mw	Quartz	211 peak
	1.54	mw	Biotite	060 peak
	1.54-1.53	w	Vermiculite	and trioct. smectite (060)
	1.53	mw	Serpentine	and talc (060)
	1.53-1.52	w	Phlogopite	060 peak
	1.52-1.49	w	Smectite	dioct. 060 peak
	1.50	m	Muscovite	and illite & attapulgite (060)
	1.49	m	Kaolinite	and halloysite (060)